

# **BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL**

## **Section A CHEMISTRY**

*Bull. Res. Council. of Israel. A. Chem.*

PROCEEDINGS OF THE XXIXth MEETING  
OF THE ISRAEL CHEMICAL SOCIETY  
Haifa, September 27-28, 1961

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- 1 Section I: Inorganic Chemistry**
- 15 Section II: Analytical Chemistry**
- 28 Section III: Physical Chemistry**
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BULLETIN  
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OF ISRAEL

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# INORGANIC CHEMISTRY

## Measurements of equilibrium constants of complexes of synthetic and natural estrogens with tetranitro-methane

SHALOM SAREL, HANNA KOWARSKY AND YEHOASHA KATZHENDLER, *School of Pharmacy, Hadassah Medical School, Jerusalem*

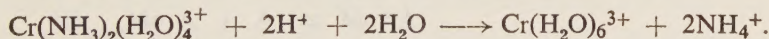
This communication reports the results of a study aimed at establishing whether the biological activities of a series of synthetic and natural estrogens can be correlated with their ability to form complexes with ligands such tetranitromethane. We have measured the equilibrium constants of stilbestrol dipropionate, dienestrol dipropionate, estradiol dipropionate, hexestrol dipropionate, with tetranitromethane in chloroform, by a spectrophotometric method developed in this study. The data at hand clearly indicate that estrogens have a low complexing power as compared with stilbene. On the other hand, this power seems to parallel the estrogenic activity.

A discussion of the method developed and data produced will be given.

## Pentaquomonoammine Cr<sup>III</sup>

BRACHA E. MAYER AND MICHAEL ARDON, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The chromic pentaquomonoammine ion  $\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{3+}$  was, until recently, the only unknown member of the series  $\text{Cr}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}^{3+}$  Ørgensen and Bjerrum<sup>1</sup> have proved its existence as an intermediate in the aquation reaction:



Traube and Lange<sup>2</sup> found that azide is reduced by  $\text{Cr}^{\text{II}}$  to ammonia:  $2\text{Cr}^{\text{II}} + 3\text{H}^+ + \text{N}_3^- \longrightarrow 2\text{Cr}^{\text{III}} + \text{NH}_3 + \text{N}_2$ . We found that one of the  $\text{Cr}^{\text{III}}$  species formed in this reaction is the chromic pentaquomonoammine ion and isolated its sulphate.

Chromous perchlorate in perchloric acid solution was added to an equivalent amount of sodium azide, in acid solution, under nitrogen. After completion of the reaction the chromic species were separated chromatographically on a sulphonated polystyrene cation exchange column by elution with  $\text{HClO}_4$ . The main products were two tripositive chromic species which were separated into two distinct bands. The more easily eluted species was identified as the hexaquo chromic ion  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . The second fraction was shown to be the monoammine  $\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{3+}$  and was isolated as the sulphate by precipitation with ethanol.



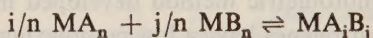
## REFERENCES

1. JØRGENSEN, E. AND BJERRUM, J., 1958, *Acta Chim. Scand.*, **12**, 1047.
2. TRAUBE, W. AND LANGE, W., 1926, *Chemisches Zentralblatt*, **I**, 1358.

### The stability of mixed ligand complexes

Y. MARCUS, *Israel Atomic Energy Commission Laboratories, Rehovoth*

The author's work on the mixed ligand halide complexes of mercury (II)<sup>1</sup> is an example of a general phenomenon of the formation of mixed ligand complexes. An examination of published values of stability constants of ternary (mixed) complexes revealed that there often is a stabilisation of the ternary complex compared with the binary complexes. In other words, the reaction



proceeds considerably to the right. If the stability of the ternary complex is measured by the free energy change for this reaction, it is found that this is made up of at least two parts. One is a statistical effect, which depends only on  $i$ ,  $j$  and  $n$ . The other is an electrostatic effect, which is due to the diminished repulsion between the ligands when they are different, compared to the repulsion in the binary complexes. This factor depends on the geometry of the complex. In some cases these two factors are sufficient to account for the free energy of stabilization.

The analogy with Bjerrum's treatment for binary complexes is pointed out.

## REFERENCE

1. MARCUS, Y., 1957, *Acta Chem. Scand.*, **11**, 329, 599, 610, 811.

### The extraction of indium chloride with triisooctylamine

D. MAYDAN, *Israel Atomic Energy Commission/Laboratories, Rehovoth*

Consider a system consisting of a solution of a long chain amine which may be considered as a liquid anion exchanger  $\text{RX}$  in an inert solvent, in equilibrium with an aqueous solution of an electrolyte  $\text{AX}$  and trace amounts of metal species  $\text{M}^{m+}$  forming anionic complexes with the anion  $\text{X}^-$  and distributed between the phases, with a distribution coefficient  $D$ . When only one complex  $\text{MX}_n^{m-n}$  ( $n > m$ ) is

dominant in the organic phase,  $\left( \frac{\partial \lg D}{\partial \lg \text{RX}} \right)_{(\text{AX}) \text{ const.}}$  will be equal to  $m-n$ .

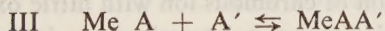
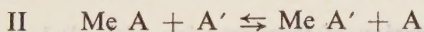
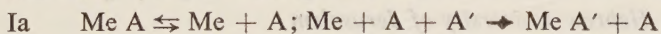
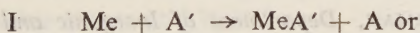
In order to determine the dominant complex  $\text{InCl}_n^{3-n}$  in the organic phase systems

comprising a solution of tri-isooctyl amine hydrochloride in xylene and aqueous hydrochloric acid with a trace amount of  $\text{In}^{3+}$  were investigated. Plots of  $\log D$  vs.  $\log(RCl)$  at constant  $\text{HCl}$  concentration up to  $1\text{M}$  resulted in curves consisting of two almost straight lines. At amine concentrations  $0.075\text{--}0.1\text{ M}$  the value of the slope is unity and at higher concentrations it is three. Results are interpreted quantitatively by assuming two indium complexes in the organic phase.  $\text{InCl}_4^-$ , at the lower amine concentrations and  $\text{InCl}_6^{3-}$  at the higher. Values of the equilibrium constants were calculated. At hydrochloric acid concentrations above  $1\text{M}$  a specific  $\text{HCl}$  effect causes a different behaviour. That is demonstrated by comparison with experiments carried out with sodium chloride at both high and low concentrations.

### The triple complexes of copper

B. KIRSON, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem.*

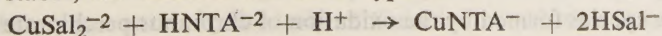
A large number of studies have been published on complexes composed either of a number of various metal ions ( $\text{Me}$ ) and only one kind of complexing agent ( $\text{Me-Me'-A}$ , where  $\text{A}$  is the complexing agent), or complexes built up from one metal ion and two different complexing agents ( $\text{Me-A-A'}$ ). Usually, no indications are given as to conditions that favour the formation of a mixed complex ( $\text{Me-A-A'}$ ), and not a mixture of complexes ( $\text{Me A}$  and  $\text{Me A'}$ ). The study of a series of omplexes of copper ( $\text{Me} = \text{copper ion}$ ) formed with various complexing agents, shows that three types of reaction between the copper ion and various complexing agents exist.



*Reaction (I) or (Ia)* will take place if the stability of the complex  $\text{MeA}'$  is much greater than that of  $\text{MeA}$ ; then the addition of a sufficient amount of the complexing agent  $\text{A}'$  will transform the complex  $\text{MeA}$  into  $\text{MeA}'$ . Copper salicylate may serve as an example when a sufficient amount of ethylenediaminetetraacetate is added to it.

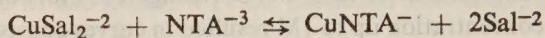
*Reaction (II)* occurs usually when the stabilities of the possible complexes  $\text{MA}$  and  $\text{MA}'$  do not differ greatly. An equilibrium between the two complexes  $\text{MA}$  and  $\text{MA}'$  may be set up also when the difference in the stabilities is not so small, but the weaker complexing agent is present in large excess. An example is the system nitriloacetate ( $\text{H}_3\text{NTA}$ ), salicylate ( $\text{Sal}$ ), copper.

In this case the equilibrium depends also on the  $p\text{H}$ . At  $p\text{H} \leq 7$ , at which the ion  $\text{HNTA}^{-2}$  is stable, the reaction will be of type I:

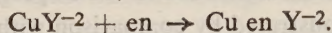
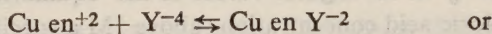




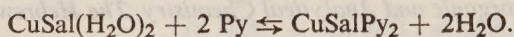
whilst at  $pH \geq 8$ , when  $NTA^{-3}$  is the stable ion, an equilibrium of type II is set up:



*Reaction III*) will occur when both of the complexing agents form stable complexes with the copper ion, e.g.:



Another method for the formation of single complexes is, of course, the substitution of a weak by a stronger complexing agent in an existing triple complex, e.g. (Py = pyridine):



It has been found that also steric effects have an influence on the formation of triple complexes.

Details of this investigation will be published elsewhere.

### Nitrosopentaquo-chromic ion

MICHAEL ARDON AND JOHN I. HERMAN, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

G. Chesneau<sup>1</sup> observed that the oxidation of chromous ion with nitric oxide results in a deep red solution, whose composition was not determined. A similar colour is obtained by the oxidation of  $Cr^{2+}$  with nitrate ion.

An investigation of this coloured solution revealed that it is a mixture of three chromic complexes. One of these, a hitherto unknown ion, causes the deep red colour of the solution.

Chromous perchlorate was oxidized with a saturated solution of nitric oxide in dilute perchloric acid. The resulting red solution was separated by means of ion exchange chromatography into three distinct components: a) the green, tetrapositive dinuclear chromic ion<sup>2</sup> b) the blue, hexaquo-chromic ion  $Cr(H_2O)_6^{3+}$  c) a deep red dipositive chromic ion which was shown to be a nitrosopentaquo-chromic ion  $Cr(H_2O)_5NO^{2+}$ . This ion was isolated as a crystalline sulphate having the composition  $[Cr(H_2O)_5NO]SO_4$ .

The chromic species formed by the oxidation of chromous perchlorate with nitrate



ion were shown to be identical with those obtained by oxidation with nitric oxide but they are produced in different proportions.

#### REFERENCES

1. CHESNEAU, G., 1899, *Compt. rend.*, **129**, 100.
2. ARDON, M. AND PLANE, R.A., 1959, *J. Am. Chem. Soc.*, **31**, 3197.

### Clay-metalorganic complexes

W. BODENHEIMER, B. KIRSON AND SH. JARIV, *Department of Inorganic Chemistry, Hebrew University and Geological Survey, Jerusalem*

#### A. OBJECT

To obtain information on structure of complexes and on clays in general and influence of cations on adsorption of complexing agents and vice versa.

#### B PRELIMINARY EXPERIMENTS

Cu-Ethylendiammine (E.D.A.) complex solutions and similar ones were instantly discoloured on addition to Wyoming Bentonite. Through ion exchange the complex returned into solution. The complex gives to the clay a characteristic colour varying with respective cation and ligand.

#### C. QUANTITATIVE EXPERIMENTS

##### *Titration*s

Na, Mg, Ca, Cu, Ni, Cd, Zn, Hg were introduced into exchange position in Wyoming Bentonite and the resulting products put in suspension and titrated potentiometrically with solutions of E.D.A. The Na, Mg, and Ca clays gave an immediate change of pH on addition of small quantities of the ammine solution. The clays with complex forming cations in the exchange position showed at the beginning of the titrations practically no changes, and only after larger additions of the ammine solution did the pH jump, indicating a distinct endpoint. In the case of Hg two such jumps were observed; the second endpoint occurred after an addition of a little more than twice the quantity added. This endpoint is common to all the cations. In the case of Ni and Cd which can form complexes 1:2, like Cu, and 1:3 unlike Cu, the endpoint is not so sharp and the pH increases gradually after the first endpoint, indicating further reactions taking place until the final pH of the ammine solution is reached. Before

reaching the endpoint, the supernating liquid does not show any reaction of ammine, proving that it has all been absorbed on the clay.

Further titrations were carried out with Cu Wyoming Bentonite using as ligands 1:2 propylene diammine 1:3 propylene diammine, 1:5 pentamethylene diammine and 1:1 hexamethylen diammine. In the case of 1:2 propylene diammine the same curve was obtained as with the E.D.A. 1:3 propylene diammine gave a curve similar to the one of Hg with E.D.A. Penta and hexamethylene diammine gave an end point equal to the first one of the Hg with E.D.A.

The first endpoint corresponds to a ratio cation: ligand 1:0.76, the second one 1:1.7.

#### *D.T.A. and T.G.*

D.T.A. and T.G. curves were taken of the clays synthesised according to the various stages of titration. The clay on which E.D.A. had been adsorbed showed mainly a strong endothermic peak at about  $130^{\circ}$ – $140^{\circ}$ , much stronger than the ordinary montmorillonite peak in this region, and two small exothermic peaks at about  $310^{\circ}$  and  $315^{\circ}$ . The Cu-clay after adsorption of E.D.A. showed first the ordinary montmorillonite peak at about  $130^{\circ}$  and then with increasing amounts of E.D.A. an increasing exothermic peak develops at about  $320^{\circ}$ . Up to a ratio of Cu: E.D.A. = 1.1 the first exothermic peak increases and the second one gradually disappears. Between 1:1 and 1:2 there appears only one exothermic peak. Beyond 1:2 the second exothermic peak gradually reappears.

Similar characteristic changes in the D.T.A. and T.G. curves were observed with the other metals showing marked changes after the final endpoint had been reached and free E.D.A. became available.

#### **The liquid volume and the solvation number of electrolytes in solution**

J. PADOVA, *Israel Atomic Energy Commission/Laboratories, Rehovoth*

From the definitions of  $\varphi_s$  the molar volume of solvated electrolyte in solution,

$$\varphi_s = \varphi_v + nV_o \quad (1)$$

$$\varphi_s = V + nV_H \quad (2)$$

where

$\varphi_v$  — apparent molar volume



$V$  — molar liquid volume of electrolyte without solvation shell

$V_o$  — molar volume of solvent

$V_H$  — molar volume of solvent in solvation shell

$n$  — solvation number of electrolyte

the concentration dependence of the solvation number is obtained, ( $k$  being a constant, and subscript  $o$  for infinite dilution).

$$n = n_o (1 - k \sqrt{c}) \quad (3)$$

which by use of the calculation of the solvation number through the apparent molar compressibility  $\varphi_K$  leads us to the liquid volume

$$V = \varphi_v - \frac{\varphi^\circ K \times S_v}{S_k} \quad (4)$$

where  $S_v$  and  $S_k$  are respectively the constants of the equations relating  $\varphi_v$  and  $\varphi_k$  to the concentration  $C$  of the electrolyte.

$$\varphi_v = \varphi_v^\circ + S_v \sqrt{c}$$

$$\varphi_k = \varphi_k^\circ + S_k \sqrt{c}$$

For anhydrous salts the alternative derivation

$$V = \varphi_v \text{ (at saturation)} \quad (5)$$

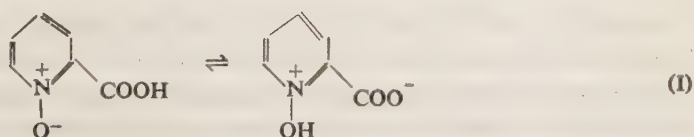
is proposed.

Values of  $V$  obtained from (4) and (5) and of  $V_H$  from (2) are checked by compressibility and density data, and compared with those taken from the literature.

### Metallic complexes of pyridine-N-oxide-2- carboxylic acid

A. HELLER, *Israel Atomic Energy Commission/Laboratories, Rehovoth*

Pyridine -N-oxide-2-carboxylic acid (PNOCA) (I) contains



the  $\equiv \text{N} - \text{O}$  group, which acts as a donor<sup>1</sup>, and the carboxylic acid group, which neutralizes the charge of the metal. Both groups can participate in a 6-member chelate ring.

As expected, stable complexes are obtained with uranyl, zirconium, beryllium, copper and ferric cations. Analysis of the compounds yielded the following compositions:  $\text{UO}_2(\text{PNOCA})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zr}(\text{OH})_3 (\text{PNOCA})$ ,  $\text{Be}(\text{PNOCA})_2$  and  $\text{Cu} (\text{PNOCA})_2$ . The solubility of the compounds was determined and it was found that only the uranyl complex is insoluble in boiling water. The complex can be precipitated also from acidic solutions below half molar in acid. The uranyl compound loses two molecules of water at  $120^\circ\text{C}$  and stays stable up to  $270^\circ\text{C}$ . This behaviour suggests gravimetric analytical applications. No insoluble compounds were obtained with a large number of other cations but no explanation could yet be found for the specificity towards the above mentioned cations.

#### REFERENCE

1. HELLER, A., 1960, *Bull. Res. Council of Israel*, 9A, 245.

### The preparation of lanthanon formates and a study of their thermal decomposition

A. GLASNER, M. STEINBERG, J. FEIGENBLATT AND W. BODENHEIMER, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Geological Survey, Jerusalem*

The formates of lanthanum, cerium, praseodymium, neodymium and samarium were prepared. The formate crystals were washed with water, followed by ethanol or acetone.

The constitution of the formates was determined by:

- (1) Calcination of the formates to the oxide  $\text{Ln}_2\text{O}_3$ .
- (2) Determination of the formate ion by titration with potassium permanganate.
- (3) Determination of carbon and hydrogen by the microanalytical method.
- (4) Absorption spectrum of the lanthanon formates in the infra red region ( $2-16\mu$ ).

Methods (3) and (4) confirmed the results obtained by methods (1) and (2). It became clear that the formate is stoichiometric. The molecule contains 0.2 moles of water per gram formula of formate. It was possible to remove the water simultaneously with the decomposition of the formate only at about  $300^\circ$  centigrade.



Thermal decompositions were carried out in the temperature range  $300^{\circ} \leq T \leq 350^{\circ}$  *in vacuum* (initial pressure  $10^{-5}$  mm). A plot of pressure versus temperature indicated the kinetics of the reaction.

The partial pressures of the gases evolved were determined. From the solid residue's weight, as well as from the infra red absorption curves, it was concluded that the residue is not the oxide  $\text{Ln}_2\text{O}_3$ , but an oxycarbonate.

Thermal decompositions were carried out by the thermogravimetric and DTA methods, under atmospheric pressure in air. The results were in satisfactory agreement with the vacuum experiments. The cerium (III) formate was an exception because of the oxidation of Ce (III) to Ce(IV).

### Studies in the thermal decomposition of europium (III) and ytterbium (III) oxalates

A. GLASNER, E. LEVY AND M. STEINBERG, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

Thermal decomposition experiments were run on dried europium (III) and ytterbium (III) oxalates. The total pressure of the evolved  $\text{CO}_2$  and CO gases was measured at different time intervals and the ratios of these two gases were determined at various time intervals and at the end of the decomposition.

In every experiment with europium (III) oxalate, the gas ratio  $\text{CO}_2/\text{CO}$  constantly decreased (e.g., at  $320^{\circ}\text{C}$ , the ratio dropped from 3.25 after 30 minutes to 2.12 after 23 hours). In many cases the  $\text{CO}_2$  obtained was more than the maximum amount which could be obtained by a decomposition to carbonate and then to the oxide<sup>1</sup>. The low temperature at which the decomposition begins, and especially the high  $\text{CO}_2/\text{CO}$  ratio, indicated a different mechanism and led us to conclude that in this reaction the europium (III) is reduced to europium (II). This conclusion was then confirmed by a spot test<sup>2</sup>.

The residues which were dark brown and signified a possibility of disproportionation of the CO, were analysed by I.R., and an attempt was made to calculate the oxalate and carbonate percentages in the residues, according to the above conclusions; the results were in good agreement with the I.R. analyses.

In the case of *ytterbium (III) oxalate*, the  $\text{CO}_2/\text{CO}$  ratios were generally equal to one, and the amount of  $\text{CO}_2$  was not much higher than the maximum expected amount. From this ratio and the colour of the light-brown residue, it was concluded that very little disproportionation had taken place.

Here too, a calculation was made of the oxalate and carbonate percentages in the residues which were found to be in almost full agreement with the I.R. analyses.

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### A new method of preparing $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>

MICHAEL SCHIEBER, *Electronics Department, The Weizmann Institute of Science, Rehovoth*

Two allotropic phases of Fe<sub>2</sub>O<sub>3</sub> are known:  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hematite with a corundum rhombohedral form and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with a spinel cubic crystal form. When heated,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is known to change monotropically to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Hematite is antiferromagnetic with a Neel point of 675°C whereas  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is ferromagnetic but with an unknown Curie point because it is unstable at higher temperatures. The principal use of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is in the production of magnetic tapes.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is generally prepared by submitting freshly precipitated Fe<sub>3</sub>O<sub>4</sub> to a prolonged annealing in an inert atmosphere of argon at temperatures between 500°C and 700°C followed by an oxidation at 200°C.

A new method of preparation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was developed which is much simpler and less time consuming.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is reduced to Fe<sub>3</sub>O<sub>4</sub> at 400°C for 30 minutes under a flow of 500 ml/minute of hydrogen saturated with water, with a partial pressure ratio of  $P_{H_2O}/P_{H_2} = \frac{1}{2}$ . The freshly formed Fe<sub>3</sub>O<sub>4</sub> is air quenched and is thus oxidized to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. That the product was  $\gamma$  was proved by X-ray powder diffractions which showed only spinelic phase lines, by analysis of divalent iron contents which were below 1% as compared to 24% in Fe<sub>3</sub>O<sub>4</sub> and by some magnetic measurements.

Oxidation of Fe<sub>3</sub>O<sub>4</sub> without a preliminary heat treatment in hydrogen or in argon<sup>1</sup> normally yields  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and not  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. These facts could be understood in view of Brown's hypothesis<sup>2</sup> that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is in fact a hydrogen ferrite with an ideal formula  $H_{\frac{1}{2}}Fe_{2\frac{1}{2}}O_4$ . Preliminary results on the hydrogen determination in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, using an oxygen combustion method<sup>3</sup> seem to agree with this assumption. About 1.9% H<sub>2</sub>O was collected by P<sub>2</sub>O<sub>5</sub> as compared to 0.4% H<sub>2</sub>O when a helium atmosphere was substituted for the oxygen. This indicates an amount of at least 0.17% H<sub>2</sub> in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as compared to 0.24% in the ideal formula  $H_{\frac{1}{2}}Fe_{2\frac{1}{2}}O_4$ . The total iron content of 69.1 $\pm$ 0.5% determined by us is also intermediate between 69.8% for Fe<sub>2</sub>O<sub>3</sub> and 68.8% for  $H_{\frac{1}{2}}Fe_{2\frac{1}{2}}O_4$ .

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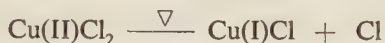
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### A new method for the preparation of colour centres

A. GLASNER AND L. BEN-DOR, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

On mixing copper chloride (II) with potassium chloride and heating the mixture in a vacuum up to 300°C, a band near 210 m $\mu$  with very high absorption appears in the spectrum of the transparent disc<sup>1</sup>. This band, attributed to the V<sub>3</sub>-centre, is probably formed as follows:



On heating to a higher temperature this band bleaches and simultaneously a second band between 250 and 270 m $\mu$  appears. This second band, which is characteristic of the copper ion, completely disappears after heating for some time at 500°C, most of the copper being oxidized to copper oxide.

V-centres were prepared also by introducing a halogen to the alkali halide at low temperatures (100–200°C). On heating to higher temperatures (~300°C) these bands bleach completely.

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### Process for production of magnesite from dolomite or limestone by reaction under pressure with magnesium chloride brines

A. BANIEL AND S. LAVIE\*, *Israel Mining Industries-Laboratories, Haifa*

Magnesium carbonate is well known in its hydrated forms; dehydration by heating does not produce the anhydrous carbonate — magnesite — but a mixture of magnesium carbonate and hydroxide.

The possibility of obtaining the anhydrous material as the only product from magnesium chloride solution and calcium carbonate was investigated. The reaction was performed in sealed tubes by heating a mixture of calcium carbonate or limestone with magnesium chloride solution or Dead-Sea End Brine (containing 250–400 g/l magnesium chloride) to 220–250°C. In some experiments dolomite was used. Somewhat higher temperatures were required in these cases.

The free volume in the tube above the slurry influenced the rate of reaction and the composition of the product obtained.

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\* Part of the work done by S. Lavie for an M.Sc. degree, under the guidance of Professor H. Heimann of the Technion. Continuation of that work entitled "Reaction between Magnesium Chloride Hexahydrate and Calcium Carbonate under Atmospheric Pressure at Elevated Temperatures" was carried out in our laboratory by O. Schaechter and R. Brosh, will be published elsewhere.

Experiments on a continuous bench scale, using direct steam as a source of heat, gave similar results.

A typical analysis of magnesite obtained from dolomite by this procedure, was:

46.4%	Magnesium oxide
0.7%	Calcium oxide
48.1%	Carbon dioxide
0.05%	Chloride

### On the interactions between ionised polymers and organic molecules

J. FEITELSON, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The interactions between polyelectrolytes and dipolar molecules or ions can be evaluated by employing a theory which describes the electrical potential in the vicinity of the polymer. We used the approach of Fuoss, Katchalsky and Lifson<sup>1</sup>, developed for rod-like molecules, and computed the purely electrostatic interactions in solution.

Dilute solutions of ionised polymers in an extended form can be approximated by highly swollen ion exchange resins (water content > 92%) and such a resin, comprising the polymer phase, was employed to test the theoretical evaluations. The distribution of molecules between the resin and the ambient solution was found experimentally by means of chromatography<sup>2</sup>. The activity coefficient ratio between the two phases was compared with the value derived from the above mentioned electrostatic considerations.

The results show that for ordinary dipolar molecules the activity coefficients can mainly be attributed to electrostatic effects, while in special cases specific group effects appear. In systems of organic ions the latter effects are more pronounced. This might, perhaps, be explained by different molecular configurations in the solution near the polymer.

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### Cation exchange with molten salts

M. LIQUORNIK, *Israel Atomic Energy Commission Laboratories, Rehovoth*

One approach to the study of molten salts chemistry, on which apparently little is known, is that of ion exchange. Owing to the relatively high temperature involved and the corrosiveness of the medium, the first problem to be solved is that of finding a material which will possess ion exchange properties and withstand the high temperature associated with the molten state. It was found that the synthetic zeolites,



"Linde molecular sieve" 4A and 13X possess these qualities. The selectivity coefficient for the sodium salt of Linde 4A and solutions of Tl nitrates in molten  $\text{NaNO}_3$  were determined. Besides ion exchange properties, these zeolites show salt inclusion. The inclusion of silver nitrate in the silver zeolite is known from the previous work of Barrer and Meier<sup>1</sup>. A simpler method to determine the inclusion was found and the inclusion of silver and sodium in the respective zeolites was checked by it.

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### Isotopic exchange by gas-liquid chromatography

J. TADMOR (TROCKER) *Israel Atomic Energy Commission/Laboratories, Rehovoth*

The applicability of the gas-liquid chromatography method to isotopic exchange between a liquid phase and a volatile inorganic compound in gaseous phase was studied.

A rapid exchange between chlorine in liquid and gaseous phase was obtained when  $\text{GeCl}_4$  and  $\text{AsCl}_3$  were eluted by the gas-liquid chromatography method in which a  $\text{Cl}^{36}$  labelled liquid phase was used.

The proposed method can be used for labelling volatile inorganic compounds by radioactive isotopes; a relatively high specific activity of the compound is obtained.

### An ion exchange study of isopolymolybdates

C. HEITNER-WIRGUIN AND R. COHEN, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The sorption of molybdates on ion exchangers was studied at various pH values and on resins of different cross-linkings. At pH values above 6,  $\text{MoO}_4^{2-}$  was sorbed while at lower pH values more condensed species are sorbed as indicated by the ratio of  $\text{Cl}^-$  desorbed to  $\text{Mo}^{6+}$  sorbed. This ratio decreases at pH lower than 3 to values of 0.36–0.41 indicating the sorption of tetramolybdate or even more condensed species. Results obtained by this method are compared with those obtained by the spectrophotometric and potentiometric methods.

### The effects of crosslinking on the selectivity of ion exchangers

Y. MARCUS AND D. MAYDAN, *Israel Atomic Energy Commission Laboratories, Rehovoth*

In the course of an investigation on the selectivity of anion exchangers towards

metal complexes, results were obtained showing the effect of crosslinking on the distribution coefficients of the metal complexes between aqueous alkali metal chloride solutions and resin phase<sup>1,2</sup>. The distribution coefficients for zinc chloride complexes were highly dependent on the crosslinking while those for similar indium chloride complexes, which differ in charge only, were almost independent of the crosslinking.

As the mean distance between the exchange sites in the resins is almost independent of the crosslinking the effect of crosslinking with the higher charged zinc chloride complex is attributed to a difference in the medium in between the sites because of the difference in the swelling of the resins. A bulk dielectric constant of the resin was calculated assuming the phase to behave as a homogenous solution of resin in water in comparison with water-dioxane mixtures. Association constants, calculated by means of the Bjerrum or Fuoss equations using these dielectric constants, show a quantitative correlation between crosslinking and selectivity of both the zinc and indium complexes.

This significant widening of the concept of bulk dielectric constant permits the calculation of the distribution coefficients from independent data.

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## ANALYTICAL CHEMISTRY

### **The application of the copper-ammonia complex to the differential spectrophotometric determination of high copper concentrations**

B. BERNAS AND M. MOSES, *Israel Mining Industries-Laboratories*

An investigation was carried out to establish optimum conditions for the application of the copper-ammonia complex as a high precision differential spectrophotometric method for the determination of copper. The purpose of this work was to develop an alternative procedure which would be less time-consuming but comparable in accuracy and precision with the electrolytic method. Although the general characteristics of the copper-ammonia complex are well known, conditions governing the requirements of differential spectrophotometry were not available to-date. The suitability of high concentrations of the copper complex was investigated and experimental conditions leading to highest precision, i.e. optimum concentration for the standard reference solution were determined. The overall accuracy and precision were found to be better than  $\pm 0.3\%$  relative.

### **Reduced pressure gas chromatography**

M. ROGOZINSKI, L.M. SHORR, AND K. JUSZKIEWICZ, *Israel Mining Industries*

The effect of vacuum on gas chromatographic analysis has been examined. Operating the column at reduced carrier gas pressure resulted in a greatly increased detector response and thus not only lowered the detection limit, but also permitted a reduction in operating temperature. Samples of tetrabromoethane containing more than ten trace impurities, representing a mixture of approximately 250° C boiling range have been satisfactorily analyzed by reduced pressure gas chromatography on silicone grease columns.

### **The use of cerous nitrate in the titration of phosphorus acids and some of their esters**

R. WARDI, *Fertilizers and Chemicals Ltd., Haifa*

The use of cerous nitrate in the alkalimetric titration of phosphoric acid and inorganic phosphates based on the reaction



is known<sup>1</sup>. It has now been found that the dibasic acids of phosphorus, i.e. mono-alkyl (or aryl) phosphoric acid, phosphorous acid and the phosphonic acids are also precipitated quantitatively by cerium (iii) ion at the pH of the first transition. In this reaction one equivalent of hydrogen ion per mol of monobasic ion of phosphorus acid is liberated which can be titrated:



The determination is carried out by titrating potentiometrically a solution or suspension of the substance in water with standard base to pH 4.7, adding the cerous nitrate solution in excess and titrating the liberated acidity again to pH 4.7. These two values together with the total phosphorous content are sufficient for the determination of a simple mixture of a phosphorous acid and its acidic esters. A more complex mixture of various acids and their esters requires in addition the determination of inorganic phosphate, total phosphite, phosphonate and neutral esters by known methods.

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### Estimation of lithium in the Dead Sea waters by flame photometry

J. YOFE AND M. STILLER, *Israel Atomic Energy Commission Laboratories*

The high concentration of cations in the Dead Sea waters produces an appreciable background to the lithium emission at  $\lambda = 670.8 \text{ m}\mu$  and also depresses its intensity.

Variations in background intensity were investigated in the range  $\lambda = 655\text{--}685 \text{ m}\mu$ , which includes the lithium emission line. For prepared solutions of a composition similar to the Dead Sea water, without lithium, readings were obtained which decreased continuously with increasing wavelength.

The background at the lithium emission line may be calculated by interpolation of the readings at  $665 \text{ m}\mu$  and  $675 \text{ m}\mu$ , since pure lithium solutions give no emission at these wavelengths.

The degree of depression of the lithium emission increases as a function of increasing total cation concentration in the solution and was measured by the use of internal standards.

Results of the analyses of 30 samples of the Dead Sea waters and brines after NaCl and carnalite precipitation are given and interpreted.



### The determination of thallium in urine\*

M. ARIEL AND D. BACH, *Department of Chemistry, Technion — Israel Institute of Technology, Haifa*

The spectrophotometric determination of thallium in urine, employing Brilliant Green, has been developed.

The thallium-Brilliant Green complex formed in the presence of the organic substrate is extracted into a toluene layer; optimal conditions for the determination are described, and the source of various interferences determined.

The method was used to check thallium excretion in the urine of patients.

### Gas-liquid chromatography of volatile metal halides

J. TADMOR (TROCKER) *Israel Atomic Energy Commission/Laboratories, Rehovoth*

A study of the elution and separation of volatile metal halides ( $\text{GeCl}_4$ ,  $\text{AsCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ ,  $\text{SnI}_4$ ) in a home made gas-liquid chromatography apparatus was performed.

Working temperatures were up to  $320^\circ$  and different stationary liquid phases ( $\text{BiCl}_3$ ,  $\text{AlBr}_3$ , silicone grease) were used.

Well defined elution peaks of the halides on  $\text{BiCl}_3$  or  $\text{AlBr}_3$  were obtained, the retention times observed being in accordance with the volatility relationship of the halides: the ratio of their retention times at a given temperature was found to be approximately the inverse of their vapour pressure ratio.

Gas-liquid chromatography was found to be suitable for the purification of the volatile metal halides from impurities at tracer level.

In the elution of a single halide on silicone grease as stationary phase, several well resolved peaks were found, possibly of reaction products between the halide and the grease.

Gas-liquid chromatography thus appears to be a suitable method of separating some (volatile) interaction products between an inorganic compound either in gaseous or liquid phase and another inorganic or organic compound.

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\* Part of a M.Sc. thesis which will be presented by D. Bach to the Senate of the Technion.

### Volumetric determination of phosphoric acid and its mono-di-and tri-esters

MARGALIT COHEN AND DAHLIA GREIDINGER, *Fertilizers and Chemicals Ltd., Haifa*

This volumetric determination of mixtures containing phosphoric acid and its various esters is based on the difference in dissociation constants between the hydrogens involved. A titration up to the first transition point ( $pH\ 4.5$ ) gives the sum of acidic components in the mixture and hence by difference the concentration of the triester can be inferred. Continuation of the titration up to the second transition point ( $pH\ 9$ ) gives the concentration of phosphoric acid and the monoester. Precipitation by silver nitrate at the first transition point liberates for titration two equivalents of hydrogen-ion per mole of phosphoric acid and one equivalent of hydrogen-ion per mole of monoester. A simple calculation based on this combined information allows for a quantitative determination of the different components.

### The determination of micro-amounts of vanadium and chromium with ortho-dianisidine in the presence of iron\*

M. ARIEL AND J. MANKA, *Department of Chemistry, Technion-Israel Institute of Technology, Haifa*

A spectrophotometric method for the determination of vanadium (+5) and chromium (+6) when present singly, in their mixtures, and in the presence of iron, exploiting the colour changes resulting from their interaction with ortho-dianisidine, has been developed.

The oxidation products of ortho-dianisidine depend on the  $pH$  of the medium employed; in 1*N* sulphuric acid its oxidation proceeds reversibly and the absorbance of the oxidized form of the reagent is quantitatively related to the concentration of vanadium (+5) and/or chromium (+6) present.

0.1 ppm of vanadium (+5) and 0.05ppm chromium (+6) may still be satisfactorily determined by this method.

### On the problem of the determination of $Ti^{++}$

C. EDEN AND H. FEILCHENFELD, *Department of Physical Chemistry, Petrochemical Laboratory of The Hebrew University of Jerusalem and The National Council for Research and Development*

One of the standard methods for the determination of the lower valence states of titanium is the titration with  $Fe^{+++}$ . This method has recently been extended to

\* Part of a M.Sc. thesis presented by J. Manka to the Senate of the Technion.



$Ti^{2+}$  or even lower states<sup>2</sup>; by allowing the titanium to react with  $Fe^{+++}$  at less than  $-40^{\circ}C$  in anhydrous ethanol oxidation of  $Ti^{2+}$  by alcohol or by water could be avoided.

The method had been developed for the investigation of Ziegler catalysts which contain possibly Ti in its lower valence states. Though this method gave correct results for a synthetic mixture of pure titanium salts we could show that it breaks down when applied to Ziegler Catalysts.

For it is not true that the alcohol at  $-40^{\circ}C$  decomposes all Al-alkyl bonds. Those which remain interfere in the determination of the lower Ti valences by participating in the reduction of  $Fe^{+++}$ .

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### A complexometric method for determination of Ba in presence of the other alkaline earths

J. YOFE, W. TULLER, R. RAFAELOF AND E. COHEN, *Israel Atomic Energy Commission Laboratories*

The stability constants of Ca, Sr and Ba complexes with EDTA are very near each other which makes the differentiation between them very difficult.

The usual method of precipitating Ba as sulphate and titration of the other two elements in the presence of a fine  $BaSO_4$  precipitate is not always exact for two reasons: (1) Some  $SrSO_4$  is coprecipitated with  $BaSO_4$  (2) The  $BaSO_4$  precipitate redissolves at  $pH = 10$  in the added EDTA during the titration of Sr and Ca. The chromate was chosen as the precipitant because of the greater difference in solubility between Ba and Sr chromates and that of sulphates.

We tried to avoid redissolution of  $BaCrO_4$  or adsorption of Sr on the  $BaCrO_4$  precipitate by using nitrobenzene to coat the surface of the precipitate. (see Volhard method for halogen titration).

#### PROCEDURE

To a mixture of  $BaCl_2$ ,  $SrCl_2$  and  $CaCl_2$  solution containing 40 to 100 micro mol of each 5 ml of buffer  $pH 10$  were added followed by 5 drops of Erio Chrome Black indicator solution (0.2% in triethanolamine) and 3 ml of Mg complexonate n/100 solution. The red solution was then titrated with a n/100 standard EDTA solution

till a blue colour appeared. This titration,  $T_1$ , is equivalent to  $\text{Ca} + \text{Sr} + \text{Ba}$ . To a second aliquot of the same volume 20 drops of nitrobenzene were added. Then a  $\text{K}_2\text{CrO}_4$  solution in an amount equivalent to the first titration, was added slowly. The colour of the solution was then yellow. It was then heated to  $70^\circ$  (for aging the  $\text{BaCrO}_4$  precipitate), cooled, 5 ml of buffer  $\text{pH} = 10$  solution, 5 drops of indicator solution and 3 ml of Mg complexonate solution added. The colour of the solution was then brownish-red. Titrate with EDTA  $n/100$  standard solution till colour change to green, second titration,  $T_2$ .

The method is rapid and amounts as low as 1 mg of Ba, Sr and Ca can be titrated accurately.

### Infinite circular gas chromatographic columns

SAMUEL SIDEMAN, *Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa*

The characteristics and performance of infinite circular columns<sup>1,2</sup> in gas chromatography have been studied. This method of operation has the following advantages:

1) The use of short circular columns instead of the usual long columns eliminates high pressure differences between outlet and inlet. 2) Absolute retention times can be read directly with no need for dead volume corrections and usually even without pressure correction. 3) Volatile solvents can be used as column coating, with practically no aging of the column. 3) Uniform coating can be made *in situ*. 5) Behaviour of ternary systems can be easily studied and separation factors applicable to extractive distillation may be evaluated.

Two mechanisms for circulating the gases in the column were constructed and compared.

The first mechanism consisted of two half "circles" with a thermal conductivity cell (T.C.C.) at each end, connected to electrically operated valves. Once the sample reached the end of a half circle, the signal from the T.C.C. triggered a specially designed relay mechanism which directed the sample gas into the second half circle and vice versa.

It was found that variations resulting from manipulation of the valves caused the peaks to broaden to such an extent that separations were not feasible.

The second mechanism consisted of a circular column with one T.C.C. connected to a variable speed pump. This arrangement was found simple to operate, though some mixing of the sample occurred during the passage through the pump section.



The effect of column efficiency as a function of "length", i.e., number of cycles has been studied theoretically and experimentally.

**ACKNOWLEDGEMENT:** Thanks are due to Mr. B. Gal-Or for his cooperation in this work and to Messrs. Z. Chouri, J. Margalit, M. Marton, E. Kutzinsky and G. Hirsh, senior students of the Department of Chemical Engineering for carrying out part of the experimental work.

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### **An approximate determination of number average DP of amylose and amylopectin in degraded starch without recourse to fractionation\***

J. SCHMORAK, D. MAJZLER AND M. LEWIN, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

The true molecular weights of both amylose and amylopectin are unknown, since, in the first place, the two components cannot be separated from each other without degradation, and, more important, their degrees of association in solvents, organic or inorganic, are unknown. For this reason it would be advantageous to obviate the necessity for fractionation, and to determine the degree of polymerization (DP) by a chemical, rather than a physical method, the former method not being affected by the solute being associated.

Such a method is provided for by the use of sodium periodate, which is a specific and stoichiometric reagent of vic-hydroxy groups (glycols). If the polysaccharide is of the 1-4'-polyanhydrohexopyranose type, then, on being quantitatively oxidized with periodate, it will consume a number of moles of periodate and it will evolve a certain number of moles of formic acid.

If the starch is randomly degraded to a certain extent — say 1 glucosidic bond scission in 500 or less AGUs — the amount of formic acid produced will be a measurable function of the molecular weight.

Mathematical formulae are deduced which allow the number-average DP of *each* molecular species to be determined with a fair degree of approximation for a randomly degraded *unfractionated* starch sample, if the amount of formic acid evolved by the sample is known.

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\* This work forms part of the research being carried out at the Institute under grant No. FG-Is-102-58 issued by the Agricultural Research Service, U.S. Department of Agriculture.

### The determination of small amounts of carbonyl groups in starch by the cyanohydrin method\*

J. SCHMORAK AND M. LEWIN, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

No standard method for the determination of carbonyl groups in starch is as yet available, but many methods have been proposed with this end in view. Some of them are merely empirical, others applicable to aldehyde and to ketone groups but *none of them applicable to small amounts of carbonyl*.

The method proposed by us consists in treating the starch with a measured excess of sodium cyanide, the latter reacting to form cyanohydrins. The unused cyanide is then determined by silver nitrate titration, after the starch has been filtered off. The method was investigated within the carbonyl concentration range from 10 to 100 anhydroglucose units per one carbonyl group, and was found to be accurate to within 5% or less.

### A colorimetric method for estimation of micro amounts of the tartaric acid isomers

JACOB YASHPHE, *Laboratory of Microbiological Chemistry, Department of Biochemistry, The Hebrew University-Hadassah Medical School, Jerusalem*

Several methods for quantitative estimation of the optical active tartaric acids are known<sup>1,2,3,4</sup>. All of these suffer from the disadvantage of being insensitive; the smallest amounts of material which can be detected being 1–3  $\mu\text{mol}$ . In the case of meso-tartaric acid only macro amounts (about 400  $\mu\text{mol}$ ) can be estimated by the existing methods<sup>4</sup>.

The method described in this paper enables estimation of all the three isomers of the tartaric acid in amounts of 0.05  $\mu\text{mol}$  or greater. The principle of the method consists of the formation of a tartrate iron ( $\text{Fe}^{++}$ ) complex, which on addition of dinitrophenylhydrazine and finally of alkali, forms a purple colour. The intensity of this colour is proportional to the amount of tartaric acid in the range of 0.05–0.4  $\mu\text{mol}$ .

Some materials interfere with the estimation of the tartaric acids by this method, including hydroxy acids, dicarboxylic acids, ethylenediamine-tetra acetate, oxidizing agents, materials which bind  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$  and possibly also other metallic ions. Nevertheless, because of the great sensitivity of the method, the dilution required to bring the tartrate concentration into the appropriate range is usually sufficient

\* This work forms part of the research being carried out at this Institute under grant No. FG-Is-102-58 issued by the Agricultural Research Service, U.S. Department of Agriculture.

to eliminate interfering effects. Phosphate ions up to  $10\mu\text{mol}$  enhance the colour intensity, possibly because of binding the  $\text{Fe}^{+++}$  ions formed; greater amounts decrease it.

Possible mechanisms by which the coloured compound is formed will be discussed.

#### DETAILS OF THE METHOD

To 1 ml sample add 2 ml of acetate buffer pH 5.4, 0.1 M; 0.1 ml of 0.015 M  $\text{Fe}(\text{NH}_4)_2\text{SO}_4$  and 0.3 ml. of 0.01M  $\text{NaH}_2\text{PO}_4$ . Make up the volume to 4 ml with distilled water. Swirl and incubate 75 minutes in a water bath at  $60^\circ\text{C}$ . Add 0.5 ml of 0.05% DNPH solution in 1N HCl and incubate 15 minutes at the same temperature. Cool in ice-water for 5 minutes and add 0.5 ml of 6N NaOH. Swirl and centrifuge for 2 minutes at 3,000 r.p.m. Read the colour intensity in a Klett-Summerson colorimeter, Filter 54.

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#### Determination of oxygen by $\text{F}^{18}$ counting in organic Li-O systems

M. ANBAR\*, M. PEISAH AND R. RAFAELOFF\*\*

The reactions  $\text{Li}^6(\text{n},\text{L})\text{t}$ ,  $\text{O}^{16}(\text{t},\text{n})\text{F}^{18}$  were used to determine the oxygen content of organic compounds<sup>1</sup>.

Using solid mixtures, lithium fluoride and the oxygen - containing organic compounds in the form of fine powders were mixed mechanically. Ratios of lithium to oxygen ranged from unity to about ten. Activities of about  $1\mu\text{c}$  for 150mg oxygen were obtained and measured by p-8 coincidence counting. Fluorine 18 yields were found to be proportional to oxygen content in the range 25–250mg oxygen. When however attempts were made to decrease the oxygen content below about 10mg difficulties were encountered due to the small oxygen impurity in lithium fluoride as well as to the competing production of fluorine-18 by the reaction  $\text{F}^{19}(\text{n},2\text{n})\text{F}^{18}$ . Of various organic solvents investigated at temperatures above their melting point, succinonitrile gave the best results. Lithium thiocyanate was dissolved in succinonitrile and the oxygen-containing organic compound was added at elevated temperatures. On cooling, the solid pellets were immersed in wax and irradiated. However,

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at oxygen contents  $< 10$  mg, the method could not be applied because of interference due to oxygen impurities in the lithium thiocyanate and the limited solubility of lithium thiocyanate in succinonitrile.

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### The determination of traces of acetylene in liquid oxygen (from 10 ppb to 5 ppm)

CH. AHARONI, *Fertilizers and Chemicals Ltd., Haifa*

Acetylene if present is a highly dangerous contaminant of liquid oxygen because of its low solubility and high flammability. Air separation plants need analytical methods sensitive up to 10 parts per billion of acetylene.

In this work acetylene is separated from the vaporised liquid oxygen by adsorption on silica gel cooled to  $-195^{\circ}\text{C}$ . Acetylene is then desorbed and concentrated by adsorption on a minute amount of similarly cooled silica gel.

"Ilosway's" reagent (ammoniacal cuprous chloride in presence of hydroxylamine) is then added to the silica gel. The highly coloured copper acetylide formed is estimated by comparing with known amounts.

The method is also suitable for the determination of traces of acetylene in air.

### A cheap and easily built gas-chromatograph

CH. AHARONI AND ERNST TH. OBERWEGER, *Fertilizers and Chemicals Ltd., Haifa*

The selfmade apparatus described is intended to analyse gases or to perform any other gas chromatographic work at room or lower temperatures.

Facilities for sample preparation are provided, allowing mixing of different gases in accurate proportions up to 99:1. Gases are manipulated with mercury - filled levelling bulbs and Orsat-type vessels. A thermal conductivity cell serves as detector and is connected to a standard recorder. High vacuum is not required.

Experiments indicate that the apparatus is reliable and accurate.

### A spectrophotometric method for the determination of chloroform

M. MANTEL, M. MOLCO AND M. STILLER, *Israel Atomic Energy Commission Laboratories*

On addition of pyridine to a chloroform solution in the presence of NaOH a reddish colour is obtained which was used by Fujiwara<sup>1</sup> and other workers<sup>2,3,4</sup> for the qualitative and quantitative determination of chloroform.

Optimal working conditions as regards, influence of NaOH concentration, effect of NaOH:H<sub>2</sub>O ratio and adequate wavelength were studied. The measurement of the absorption spectrum included the ultraviolet range. Except the already known maximum <sup>2,3,4</sup> at 525 m $\mu$  a second higher one appears at 366 m $\mu$ .

After 24 hours — when the solution was colourless — the maximum in the visible disappeared while the maximum in the ultraviolet persisted and was higher.

By plotting calibration curves in the range from 0.2 to 5  $\gamma$ /ml chloroform it was found that Beer's law was obeyed also in the ultraviolet.

The sensitivity of the reaction was increased 50 times by working in the optimal conditions established, permitting the detection of 0.043  $\gamma$ /cm<sup>2</sup> for a difference of 0.01 in absorbancy at  $\lambda = 366$  m $\mu$  after complete decoloration of the red product originally studied by Fujiwara.

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### Quantitative determination of free sulphur in hydrocarbons by the benzoin method

A.B. STERN AND M. BABITZ, *Chemical Testing Laboratory, Technion-Israel Institute of Technology, Haifa*

Free sulphur reacts with benzoin, giving H<sub>2</sub>S according to the following reaction:



The H<sub>2</sub>S is transferred to an absorption vessel containing a solution of Cd(OH)<sub>2</sub> and determined colorimetrically as methylene blue on a Lovibond tintometer, or on a spectrophotometer at 670 m $\mu$  wavelength.

In the present study optimum conditions for the reaction were determined and a simple apparatus proposed for this purpose.

It was found that at 180°C (measured in the bath) conversion is quantitative. The minimum detectable sulphur content is 0.5  $\gamma$  and the required volume of solution ranges from 0.5 to 5 ml. The influence of other sulphur compounds occurring in petroleum fractions (mercaptans, organic sulphides, disulphides etc.) was also studied, and it was established that these compounds do not interfere with the determination. Olefinic sulphur derivatives, however, undergo partial decomposition at that temperature, with the liberation of sulphur which takes part in the reaction.

The detection of free sulphur in various straight-run, cracked and aviation gasolines was also studied. In cracked gasoline it was still detectable even after preliminary removal with mercury; this is attributed to the decomposition of olefinic sulphur compounds.

The ordinary micro-quantitative methods for determination of sulphur in gasoline are mostly colorimetric and thus impracticable whenever the gasoline contains an organic dye. The method developed by the authors, however, permits determination of sulphur even in dyed gasolines.

### **Organization of gas chromatography literature for storage and retrieval by the "uni-term" system of co-ordinate indexing**

M. ROGOZINSKI AND M. MEDWIED, *Israel Mining Industries-Laboratoires, Haifa*

In our laboratories 1500 abstracts have been collected to date on Gas Chromatography. The number of abstracts continues to grow exponentially. Searching for relevant information became tedious and time consuming. Therefore the contents of the literature represented by the abstracts were organized by the "Uni-term" system of co-ordinate indexing. In this system the content of a separate literature item is related to a group of logical terms (or concepts) the combination of which by a simple system of logical rules gives the searched for complex idea. By the method of trial and error, we obtained a high degree of precision in retrieving the sought for information. A small thesaurus on Gas Chromatography has been developed. It serves as the basis for continuous definition of the literature stored by uniterms. The system consists by now of about 350 terms, which are sufficient to cover the whole subject field. Definition of uniterms, examples of retrieval and the intellectual aspects of the subject field vis uniterm coordinate indexing system will be discussed.

### **Determination of small quantities of tellurium in the presence of very large quantities of bismuth.**

S. GOREN, M. MANTEL AND M. STILLER, *Israel Atomic Energy Commission Laboratories*

#### **SPECTROPHOTOMETRIC METHOD**

A tellurium sol is obtained by reduction of the  $\text{Te}^{\text{LV}}$  to metallic Te by stannous chloride in hydrochloric acid solution<sup>1</sup>.

Optimal working conditions as regards: acid normality,  $\text{SnCl}_2$  concentration, period of sol stability and adequate wavelength, were studied, as well as maximum permissible bismuth concentration.

The absorption of the sol at  $\gamma = 400 \text{ m}\mu$  was measured directly without prior separation of the bismuth.



The limit of sensitivity was found to be 0.2  $\gamma$ /ml of Te.

The accuracy is 0.3%.

#### CHROMATOGRAPHIC METHOD

Using a solvent mixture of 2 parts isopropyl ether, 2 parts 96% ethanol and 1 part concentrated hydrochloric acid, the tellurium was raised on a chromatostrip<sup>2</sup>.

R<sub>F</sub> value obtained for Te is 0.9

R<sub>F</sub> value obtained for Bi is 0.7

By spraying the chromatogram with an acidic solution of SnCl<sub>2</sub> only one dark spot is obtained. This spot corresponds to metallic Te, which is the result of reduction to the elementary state.

0.15 amounts of Te could be detected on the chromatostrip in the presence of thousandfold quantities of bismuth.

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# PHYSICAL CHEMISTRY

## The decomposition of $\text{H}_2\text{O}_2$ solutions by atomic hydrogen

G. CZAPSKI, J. JORTNER AND G. STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The reactivity of atomic hydrogen generated by an electrodeless discharge in dilute aqueous  $\text{H}_2\text{O}_2$  solutions was investigated. Atomic hydrogen reacts with  $10^{-4}$ – $10^{-5}$  M  $\text{H}_2\text{O}_2$  solutions with a rate constant of  $k \sim 10^5$  liter  $\text{mol}^{-1}$   $\text{sec}^{-1}$ . This reaction is compared with those postulated for the radiolysis of aqueous  $\text{H}_2\text{O}_2$  solutions<sup>1</sup>. In irradiated solutions two forms of H atom equivalent are present<sup>1,2</sup>, exhibiting different reactivity with specific scavengers, e.g.  $\text{H}_2\text{O}_2$ . Our results indicate that the pair of reactive species in irradiated aqueous solutions is the solvated electron and the H atom.

The comparative study of radiation chemical reactions with the reactivity of atomic hydrogen yields information on the basic mechanisms in the radiolysis of water.

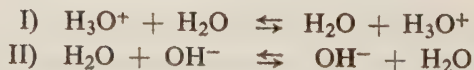
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## Activation energies of proton transfer reactions in water

A. LOEWENSTEIN AND A. SZOKE, *Nuclear Magnetic Resonance Department, The Weizmann Institute of Science, Rehovoth*

Many fast proton transfer reactions have recently been studied by the nuclear magnetic resonance technique. The rate constants for the reactions:



were measured by Meiboom<sup>1</sup> and were found in good agreement with the anomalous mobilities of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions.

In this work the activation energies of these reactions were measured and found to be:

$\Delta E = 2.6 \pm 0.3$  Kcal/mole and  $\Delta E = 5.2 \pm 0.6$  Kcal/mole for reactions I and II respectively. The values are in accordance with theoretical considerations<sup>2</sup> on the nature of these reactions.

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### Comparison between the exchange reaction of the phosphorus bonded hydrogen of dialkyl phosphonates and the oxidation of these compounds

B. SILVER AND Z. LUZ, *The Weizmann Institute of Science, Rehovoth*

The kinetics of oxidation of dialkyl phosphonates was studied by Nylen<sup>1</sup> and was found to be general acid and general base catalyzed. The general expression for the specific rate of oxidation may be written:

$$k = \frac{R}{[(RO)_2PO.H]} = k_w + k_{H^+}[H^+] + k_{HA}[HA] + k_{OH^-}[OH^-] + k_{B^-}[B^-] \quad (1)$$

The exchange of the phosphorus bonded hydrogen in dialkyl phosphonates with solvent D<sub>2</sub>O was studied by observing the changes in the relevant lines of the N.M.R. spectra as a function of time. In addition to a spontaneous reaction the reaction was found to be catalyzed by DCl, CH<sub>3</sub>COOD and by sodium acetate. The results can be expressed in terms of an expression similar to equation (1). The catalytic constants  $k_w$ ,  $k_{H^+}$  and  $k_{AcO^-}$  for the exchange were obtained and found to have values similar to the corresponding catalytic constants for the oxidation reaction.

On the basis of these results it is suggested that the oxidation and exchange reactions proceed via a common intermediate, the formation of which is the rate determining step in both reactions. This intermediate is probably the phosphite form<sup>2</sup> [(RO)<sub>2</sub>P.OH] of the phosphonate [(RO)<sub>2</sub>PO.H], since this form is very reactive, rapidly reverting to the phosphonate form, or being oxidized in the presence of an oxidizing agent.

The breaking of the P-H bond was shown to be rate determining for acid catalysis, since a large kinetic isotope effect ( $k^H/k^D = 4$ ) was found for oxidation. For acetate ion catalysis the very small isotope effect found indicates that the transition state is formed by direct attack of acetate ion on the phosphorus atom.

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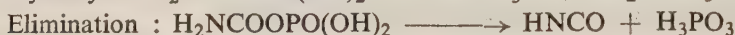
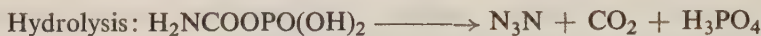
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## Kinetic and tracer studies in the hydrolytic and elimination reactions of carbamoyl phosphate

M. HALMANN, A. LAPIDOT AND DAVID SAMUEL, *Isotope Department, Weizmann Institute of Science, Rehovoth*

Carbamoyl phosphate in acid solution undergoes hydrolysis, forming carbon dioxide, ammonia and orthophosphate. This reaction occurs with the monoanion, the neutral molecule, and the conjugate acid of carbamoyl phosphate. The dianion of carbamoyl phosphate and its conjugate base undergo elimination, forming isocyanate and orthophosphate.



Mechanistic details of these reactions were studied (a) by measuring the point of fission of the C–O–P bond, using  $\text{O}^{18}$  enriched water, and (b) by determining the solvent isotope effect on the rates of these reactions in deuterium oxide. Results are given in the following table:

	Conjugate acid	Neutral molecule	Monoanion	Dianion	Conjugate base
Charge state	+1	0	−1	−2	−3
Rate constant $10^4(\text{sec}^{-1})$	$k_A = 3.1$	$k_o = 0.55$	$k_1 = 0.505$	$k_2 = 0.5$	$k_B = 0.364 \times 10^4$ (lit. $\text{ml}^{-1} \text{sec}^{-1}$ )
$k_H/k_D$	1.0	1.0	1.34	1.0	1.3
%P–O bond fission	5	15	23	1	1

This investigation was supported in part by a research grant RG-5842 of the U.S. Public Health Service.

## Cryoscopy of anions in perchloric acid solutions

MICHAEL ARDON, *Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem*

The system  $\text{HClO}_4 - \text{H}_2\text{O}$  has an eutectic point at a perchloric acid concentration of 40.7% consisting of ice and a perchloric acid hydrate of unknown composition  $\text{HClO}_4 \cdot x\text{H}_2\text{O}^1$ .

This solution has a freezing point of  $-59.7^\circ\text{C}^1$ .

Foreign electrolytes dissolved in a eutectic solvent of this type lower its freezing point by an amount which depends only on the concentration of the foreign ions and is not dependent on the ions which are common to the solute and the solvent<sup>2</sup>. The eutectic solution of 40.7% perchloric acid was used as a solvent for a number of metallic perchlorates ranging from divalent to tetravalent and the mean value for the molal depression of the freezing point was determined<sup>3</sup>.

The same solvent was used for M.W. determinations of anions of various acids. In this case, only the foreign anion will lower the freezing point of the solvent, while the hydrogen ion will be ineffective. The following results were obtained:

Solute	Range of Molalities	$K_f$
HCl	0.0155 to 0.0465	4.02
HClO <sub>3</sub>	0.0176	3.92
H <sub>2</sub> SO <sub>4</sub>	0.0165 to 0.0330	4.12
HNO <sub>3</sub>	0.0198 to 0.0985	2.06

The  $K_f$  values for  $\text{Cl}^-$ ,  $\text{HSO}_4^-$  and  $\text{ClO}_3^-$  are only slightly lower than those obtained for divalent cations<sup>3</sup>, but the value for  $\text{HNO}_3$  is one half of that value. This result seems to indicate the existence of a nitric dimer in perchloric acid solutions. No other evidence was found for the existence of nitric dimers in dilute solutions.

An alternative, though less plausible explanation, is the assumption of a solid solution with a nitrate distribution coefficient  $k = 0.5$  between the solid and liquid phase.

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### The decomposition of the aluminum-carbon bond by carbon tetrachloride

C. EDEN AND H. FEILCHENFELD, *Department of Physical Chemistry, Petrochemical Laboratory of The Hebrew University of Jerusalem and The National Council for Research and Development*

The reaction of triethylaluminum with  $\text{TiCl}_4$  or  $\text{TiCl}_3$  in  $\text{CCl}_4$  was investigated. The system behaved like a normal Ziegler catalyst during an induction period of several hours and then decomposed spontaneously. The induction period was shortened by decreasing the ratio of  $\text{Al}(\text{C}_2\text{H}_5)_3$  to  $\text{TiCl}_4$ , by using smaller amounts of  $\text{CCl}_4$  and by raising the temperature.

It was shown that in the absence of  $\text{TiCl}_4$  neither  $\text{Al}(\text{C}_2\text{H}_5)_3$  nor  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  were decomposed by  $\text{CCl}_4$ ; however  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$  and  $\text{CCl}_4$  reacted spontaneously. A carbonium ion mechanism based on the intermediate  $\text{C}_2\text{H}_5^+ \text{AlCl}_4^-$  is proposed. All the major reaction products which would be expected from such a mechanism have actually been found. This is in contrast to the more usual carbanionic and free radical mechanisms established for the decomposition of the metal carbon bond.

### The interaction of OH free radicals with iodoaromatic compounds

M. ANBAR AND MIRIAM BOBELSKY, *Isotope Department, Weizmann Institute of Science, Rehovoth and Israel Atomic Energy Commission/Laboratories, Rehovoth*

The interaction between OH free radicals formed by Fenton's reaction with iodoaromatic compounds has been investigated. The deiodination reaction of o-iodophenetole sulphonate has been followed in the presence of various inorganic and organic compounds, which competed for the OH free radicals. The relative rates of interaction of OH radicals with various compounds have been derived. It was suggested that the mechanism of reaction involves an electron transfer from the aromatic nucleus to the free radical; comparable results were obtained with OH free radicals generated by X-rays in aqueous solutions.

### Reduction of $\text{TiCl}_4$ by Na on alumina

H. FEILCHENFELD AND D. ZEHAVID *Department of Physical Chemistry, Petrochemical Laboratory of The Hebrew University of Jerusalem and the National Council for Research and Development*

It has been stated that between 125 and 200°C a Na on alumina dispersion reduces  $\text{TiCl}_4$  to metallic Ti<sup>0</sup>. When we used, however, a Li on alumina dispersion only violet  $\text{TiCl}_3$  was produced. This raised doubts whether the black product obtained with the Na dispersion was in fact metallic Ti or rather  $\text{TiCl}_2$ . Since these dispersions have catalytic properties, the question has considerable theoretical interest.

The distinction between  $\text{TiCl}_2 + 2\text{Na}$  and  $\text{Ti}^0$  is not straightforward. It was however possible to solve the problem by first decomposing the  $\text{TiCl}_2$  and Na by hot NaOH solution and analyzing for the remaining  $\text{Ti}^0$  after dissolving it in hot HCl by titration with  $\text{Fe}^{+++}$ .

If  $a$  = moles  $\text{H}_2$  liberated on dissolving  $\text{Ti}^0$

$b$  = g-equiv. Ti titrated

then the amount of metallic Ti is: 
$$c = \frac{2a + b}{4}$$

It could in this way be shown that the Na-dispersion reduces  $\text{TiCl}_4$  only to  $\text{TiCl}_2$ .  $\text{Ti}^0$  appears only when the mixture is heated to above 400°C.

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## Equilibrium studies in the system $\text{H}_2\text{SO}_4\text{-HCl-nBuOH-H}_2\text{O}$

R. BLUMBERG, P. LEWI AND P. MELZER, *Israel Mining Industries-Laboratories, Haifa*

The equilibrium system  $\text{H}_2\text{SO}_4\text{-HCl-nBuOH-H}_2\text{O}$  was investigated and equilibrium data were determined in those regions where two liquid phases coexist.

The individual distributions of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{H}_2\text{O}$  between the two phases and the dependent interrelationships were determined over a wide range of concentrations.

For simplification purposes the data were determined at three different relations of  $\text{H}_2\text{SO}_4\text{:HCl}$ , namely: 1:1, 1.5:1, 3:1.

It was found that the system can be presented as a family of ternary curves with the sum,  $\text{H}_2\text{SO}_4 + \text{HCl}$ , as one of the apices. Each curve represents a definite  $\text{H}_2\text{SO}_4\text{:HCl}$  ratio, and the curves lie between the two ternaries:  $\text{H}_2\text{SO}_4\text{-nBuOH-H}_2\text{O}$  and  $\text{HCl-nBuOH-H}_2\text{O}$ .

On correlating the tie-lines by the method of Treybal<sup>1</sup> a family of straight lines was obtained that lies between the lines representing the correlations for the respective ternary systems.

Among the many correlations obtained in the quaternary system it was found that:

There is a linear relation between the ratio  $\text{H}_2\text{SO}_4\text{:HCl}$  in the alcoholic phase to that in the aqueous phase.

A single straight line represents the partition coefficient  $K_{\text{HClalc/aq}}$  as a function of the total acidity in the aqueous phase — for all the ratios  $\text{H}_2\text{SO}_4\text{:HCl}$  examined.

The relationship  $K_{\text{H}^+ \text{alc/aq}}/\text{total acidity}$  in aqueous phase is represented by a family of straight lines corresponding to each of the ratios  $\text{H}_2\text{SO}_4\text{:HCl}$ . The lower the ratio  $\text{H}_2\text{SO}_4\text{:HCl}$  in the aqueous phase, the higher the water transfer to the alcoholic layer.

At a given total acidity in the alcoholic phase, the water concentration increases with decreasing ratio of  $\text{H}_2\text{SO}_4\text{:HCl}$ .

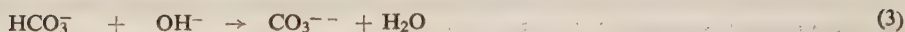
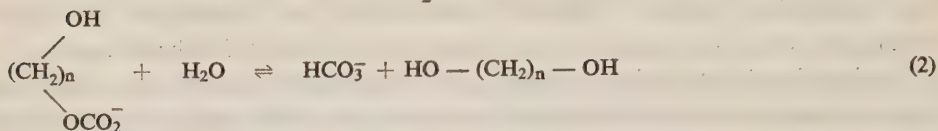
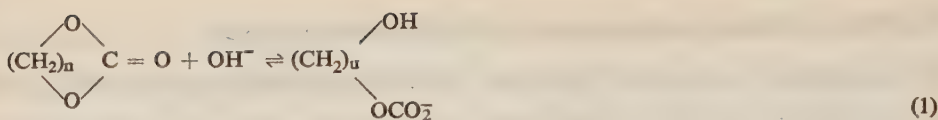
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## Kinetics of alkaline hydrolysis of ethylene carbonate

YEHOSHUA KATZHENDLER, LEO A. POHORYLES AND SHALOM SAREL, *Department of Pharmaceutical Chemistry, The Hebrew University of Jerusalem*

It has already been shown<sup>1</sup> that the hydrolysis of cyclic carbonates in alkali is a two stage process. The first stage, which follows second-order kinetics, is followed by a slow first-order reaction.



This study is concerned with measuring the rates and equilibrium constants of both stages of hydrolysis of ethylene carbonate. We found that the equilibrium constant of the first stage of the reaction can be calculated by expression (4) which was developed in this study.

$$\ln A_0/A = t(K_2.k_3)/K_2 + 1 \quad (4)$$

Where  $A_0$  is the initial concentration of ethylene carbonate,  $A$  that concentration at time  $t$ ,  $K_2 = K_{eq} \times (\text{OH}^-)$ , and  $t$  time. The first order rate constant of the second stage of hydrolysis,  $k_3$ , was measured independently by running the reaction in a great excess of alkali and the extent of reaction was determined from the production of inorganic carbonate during the reaction.

A description of the experimental method and mode of calculation will be given.

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#### Studies on the isotopic exchange of gaseous hydrogen with liquid aliphatic amines

K. BAR-ELI AND F.S. KLEIN, *Isotope Department, Weizmann Institute of Science, Rehovoth*

The exchange of gaseous hydrogen and liquid ammonia was studied extensively and described in the last conference<sup>1</sup>.

In the present work the exchange of gaseous hydrogen with liquid aliphatic amines was studied. This exchange is catalysed by both unsubstituted and substituted alkali amides. The substituted amides were shown to be much more active catalysts. In fact a value of more than 35 was found for the ratio of the catalytic activity of potassium methylamide and potassium amide at  $-66.2^\circ\text{C}$ . At higher temperatures this value decreases, as should be expected, because lower energies of activation were found in the case of exchanging amines than in ammonia: methylamide has an activation energy of  $6.8 \pm 0.2$  Kcal/mol while that for amide is  $10.2 \pm 0.3$  Kcal/mol.

It is interesting to note, that much higher ( $>20$  Kcal/mol) activation energies were found in the case, of the analogous base catalysed hydrogen exchanges of the oxygen system of compounds, i.e. water and methyl alcohol<sup>2</sup>.

The exchange rate was shown to be proportional to the concentration of the undissociated catalyst molecule with some contribution from the ion. Lack of data for the dissociation constants of alkali amides in amines did not allow for this contribution to be estimated.

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### The mechanism of chloramine hydrolysis in alkaline solutions

M. ANUBAR AND G. YAGIL, *Isotope Department, Weizmann Institute of Science, Rehovoth*

The hydrolysis of chloramine and of dimethylchloramine was investigated in alkaline solutions from  $pH = 12$  to 12 molar NaOH. The hydrolysis which produces hydroxylamine as the primary product was found first order in chloramine and showed a linear dependence on the  $H$ -acidity function. It was found that the hydrolysis of deuterated chloramine proceeds faster than that of chloramine, and the hydrogen exchange between water and dimethylchloramine proceeds slower than the rate of hydrolysis. These as well as other results suggest the nucleophilic substitution of chloride by a hydroxyl ion as the most probable mechanism of hydrolysis.

### The kinetics of the oxidation of ethanol and of acetaldehyde by bromine. Influence of $pH$

B. PERLMUTTER-HAYMAN AND Y. WEISSMAN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

In the oxidation of ethanol by bromine water the oxidant is molecular bromine, and not HOBr or  $Br_3^-$ . The reaction proceeds in two steps<sup>1</sup>, viz:



In order to investigate the kinetics of the oxidation of ethanol, we therefore first of all had to investigate reaction 2.

At low values of  $pH$ , both reactions were found unaffected by changes in  $pH$ ; at higher values, the rate gradually increased until finally the rate increased linearly with the  $OH^-$  concentration.



An analogous behaviour had been found previously for the oxidation of glucose<sup>2</sup> and of formic acid,<sup>3</sup> and was explained on the assumption that the organic substance reacts in the form of its anion. If the same explanation is valid in the present case, the aldehyde has to react as the anion of its hydrate.

The proposed mechanism is in good agreement with a mechanism proposed recently<sup>4</sup> on the basis of the kinetic isotope effect.

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### The detailed mechanism of the hydrolysis of chlorine

ASSA LIFSHITZ AND B. PERLMUTTER-HAYMAN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

Last year<sup>1</sup>, we reported on the kinetics of the hydrolysis of chlorine in pure water<sup>2</sup>, and in the presence of acetate<sup>3</sup>. This time, results in the presence of various other anions of weak acids are presented. A correlation is shown to exist between the rate constants and the dissociation constants of the acid. This correlation allows a deeper insight into the actual mechanism of the reaction. Various possibilities are discussed. The two mechanisms which are compatible with all the known facts are analyzed in detail. According to one of these mechanisms, the reaction takes place in a single step, whereas the other involves rate determining proton transfer.

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### Reactions of the aquated electron in irradiated waters solutions

C. LIFSHITZ, J. RABANI AND G. STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The difference between the reactions undergone by  $e_{aq}^-$  and H atoms<sup>1</sup> was further investigated in the present work. Hydrogen yields from irradiated formate solutions were determined.  $G(H_2) = 1.5$  in neutral concentrated ( $10^{-1}M$ ) formate solutions. This value is lower than the sum:  $g(H) + g(H_2) \cong 3.3$ . If the pH is adjusted with phosphate instead of base,  $G(H_2) = 3.3$ . At pH = 4.3,  $G(\text{hydrogen}) = G(D_2) + G(HD) = 1.8$  for a  $D_2O$  - formate solution compared with  $G(H_2) = 2.5$  for  $H_2O$ . At the same pH,  $G(H_2) = 3.7$  for  $10^{-3}M$  formate, in agreement with previous

results<sup>4</sup>. By means of isotopic labelling this high molecular hydrogen yield was found to have its origin in the water only.

By measuring hydrogen yields in the system formate-acetone-ferricyanide,

$$\frac{k_{\text{H}} + \text{Fe}(\text{CN})_6^{-3}}{k_{\text{H}} + \text{HCOO}^-}$$

was found equal to  $\sim 20$  ( $p\text{H} = 7.6$ ), in agreement with the value found for  $p\text{H} = 1.2 - 2.5$ <sup>(3)</sup>.

These results indicate that the basic and acidic forms of the H radical occurring in irradiated water are  $e_{\text{aq}}^-$  and H, respectively. Hydrogen atoms yield molecular hydrogen, as a product of their reaction with  $\text{HCOO}^-$ , while electrons are captured by high concentrations of this ion yielding no hydrogen whatsoever.

The aquated electron is supposed to be more stable in heavy than in light water<sup>4</sup>. It is therefore possible that the contribution of electron scavenging by the formate is higher in heavy than in light water.

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#### The oxidative degradation of cotton by hypochlorite\*

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Functional groups and degradation of cotton oxidized by hypochlorite at several  $p\text{H}$  values (5–10) were studied.

The carboxyl group content of the oxidized cottons increases while the aldehyde and ketone groups content decreases with increase in  $p\text{H}$ . Approximately 40% of the oxidant consumed is accounted for by the functional groups at all  $p\text{H}$  values. The ratio of carboxyl, aldehyde and ketone groups formed per scission is 1–1.5–3.5 at the acidic  $p\text{H}$  range and 5–0.8–0.0 at  $p\text{H}$  10. Twenty six atoms of oxygen are consumed per scission out of which 10.4 atoms are accounted for by the functional groups. The rest of the oxygen is explained by oxidation of the soluble products of the short chain material in the fibre phase and by the functional groups of the short chains with D.P. up to 37.

\* This work forms part of the research being carried out at the Institute under grant No. FG-Is-101-58 issued by the Agricultural Research Service, U.S. Dept. of Agriculture.

The degradation was found to be random in the whole pH range studied as proved by the ratio of the number average and weight average molecular weights and by the linearity of the plot of log intrinsic viscosity versus log consumed oxygen<sup>1</sup>.

Earlier studies<sup>2</sup> indicated that the reaction proceeds by a free radical mechanism.

It is further suggested that the degradation and oxidation reactions occur simultaneously at a given pH with similar rates, so that all carbon atoms of an anhydro-glucose unit in all chains of the amorphous phase will have a similar probability of being attacked.

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### Charge transfer spectra of oxygen in solution

J. JORTNER AND U. SOKOLOV, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

Oxygen solutions in water, alcohols, nitriles, aromatic and aliphatic hydrocarbons give rise to continuous absorption bands<sup>1,2</sup>. The apparent molar absorption coefficients of O<sub>2</sub> in solution were found to be independent of oxygen concentration. These absorption bands are assigned to charge transfer spectra, the oxygen acting as an electron acceptor. This is consistent with the intensity of the bands and the dependence on the nature of the solvent. A linear correlation was observed between the band onset energies and the ionization potentials of the solvent molecules.

Application of these data leads to a spectroscopic estimation of the electron affinity of O<sub>2</sub>, in good agreement with thermal data<sup>3</sup>.

Analysis of thermochemical data for the solubility of O<sub>2</sub> indicates that there is no thermochemical evidence for complex formation in these systems. These bands are due to contact charge transfer<sup>4</sup>.

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### Photochemistry of the I<sup>-</sup> ion in aqueous solutions

J. JORTNER, M. OTTOLENGHI AND G. STEIN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

We reported recently<sup>1</sup> our results on the dependence of the quantum yields in an evacuated KI solution on pH, I<sup>-</sup> concentration and light intensity. The experimental results



for this system were treated by a diffusion controlled scavenging mechanism from a photochemical cage<sup>2</sup>. The nature of the scavenged species and the mechanism of this process were further investigated. Various scavengers e.g.  $H^+$ , aliphatic alcohols, nitrous oxide and oxygen were employed. At high scavenger concentrations a limiting quantum yield  $0.290 \pm 0.005$  at  $25^\circ C$  was observed, independent of the nature of the scavenger. Application of specific scavengers made possible discrimination between

H atoms and their precursors formed from the dissociation of the excited state of the ions  $H^+$  and  $N_2O$  sense as efficient scavengers for solvated electrons, while alcohols scavenge H atoms. The dependence of the quantum yield on the scavenger concentration was found to be in good agreement with a general equation derived by us for diffusion controlled scavenging.

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### The absorption spectrum of $NO_3^-$ in solution

D. MEYERSTEIN AND A. TREININ, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The electronic spectrum of  $NO_3^-$  is characterised by two absorption bands, one of low intensity,  $\lambda_{max}$  at about  $300 m\mu$ , and the other of high intensity at about  $200 m\mu$ . While the weak band is generally attributed to intramolecular transition, probably a forbidden  $n \rightarrow \pi^*$  transition, there are still conflicting views on the nature of the high intensity transition. Environmental effects were studied by us as a tool to ascertain the type of this transition. By changing temperature, solvent and adding various foreign solutes we detected effects which are entirely different from those displayed by electron-transfer spectra<sup>1</sup>. Hence this band is assigned to internal transition, probably  $\pi \rightarrow \pi^*$ .

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1. STEIN AND TREININ, 1959, *Trans. Faraday Soc.*, **55**, 1091; *ibid*, 1960, **56**, 1393.

### Infrared spectrum of $NH_3$ adsorbed on chlorinated porous Vycor glass

M. FOLMAN, *Department of Chemistry, Technion-Israel Institute of Technology, Haifa*

Adsorption of  $NH_3$  on chlorinated porous Vycor glass was studied by means of infrared spectra<sup>1</sup>. After the removal of most of the surface OH groups,  $NH_3$  was adsorbed and its infrared spectrum recorded. Strong absorption bands at  $3520 cm^{-1}$  and  $3445 cm^{-1}$  were observed. These bands remained unchanged after desorption of the ammonia by evacuation and heating to  $450^\circ C$ . The two bands have been

ascribed to stretching frequencies of  $\text{NH}_2$  groups formed on the surface. Three other absorption bands at  $3150\text{ cm}^{-1}$ ,  $3050\text{ cm}^{-1}$  and  $2805\text{ cm}^{-1}$  which disappeared on desorption at  $200^\circ\text{C}$  were found being due to  $\text{NH}_4^+$  ions present on the surface during the process of amination as  $\text{NH}_4\text{Cl}$ . The  $\text{NH}_4\text{Cl}$  exists on the surface most probably as single molecules.

Two weak absorption bands at  $3380\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  are due to adsorbed  $\text{NH}_3$ . They disappear after heating and evacuation fairly quickly, indicating that the surface bond is not strong and the molecule is adsorbed physically.

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### Medium effects on atomic energy levels

J. JORTNER, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

Environmental effects on the ground state charge distribution and the energy levels of an atom are treated by application of a continuous dielectric model for the medium<sup>1</sup>. The present application of this model is based on the Hartree Fock approximation for the electronic wave function of the whole system. The effect of the medium polarization was computed by a restricted self consistent field variation and perturbation treatments. The medium dielectric effects were compared with the results based on molecular models, taking into account dispersion and repulsion-overlap forces. Dielectric effects on Rydberg type electronic transition lead to blue spectral shifts which are equivalent to the effect of long range repulsion forces. This conclusion is supported by recent experimental evidence<sup>2,3</sup>.

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### A critical discussion of the spectrophotometric method of determining association constants of 1:1 complexes

H.J.G. HAYMAN, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The methods available for determining association constants of 1:1 complexes by the spectrophotometric method will be reviewed briefly. The effect of the presence of complexes of other compositions, of non-ideality of the solutions, and of the existence of "contact absorption" will be considered. The possible bearing which these factors may have on the lack of agreement often found between association constants determined by the spectrophotometric and partition methods will be discussed.

## Nuclear magnetic resonance studies of adsorbed molecules

D. FIAT, *Isotope Department, The Weizmann Institute of Science*

Using a Varian 60 M.C. high resolution N.M.R. spectrometer, proton relaxation times of methanol adsorbed on porous vycor glass were measured and calculated. At present measurements of  $\text{NH}_3$  adsorbed on the same adsorbent are in progress. It was possible to measure and calculate the relaxation times at surface cover ages as low as  $\theta=0.025$  ( $\theta$ =fraction of monolayer) where the amount adsorbed was approximately  $5 \times 10^{-4}$  expressed as gram atoms of hydrogen. The measurements extended up to  $\theta \sim 3$ . The relaxation times were calculated from the peak height and width of the  $\nu$ -mode line as a function of the radio frequency field  $H_1$  under conditions of slow passage<sup>1</sup>. The radio frequency field  $H_1$  was measured using Anderson's method<sup>2</sup>.  $T_2$  versus amount adsorbed shows a point of inflection at  $\theta=0.2$ . Up to this point the slope increases and then decreases. After completion of the first layer a further change in slope occurs. At  $\theta=0.025$ ,  $T_2=0.15$  milliseconds. At monolayer  $T_2=3.5$  milliseconds.  $T_1$  versus amount adsorbed reveals a minimum at  $\theta \sim 0.2$  and increases gradually up to  $\theta=1$ . From  $\theta=1$  there is a sudden increase in the slope. At  $\theta=0.025$   $T_1=450$  milliseconds. The minimum value of  $T_1$  at  $\theta \sim 0.2$  is 37 milliseconds. The results:  $1 > T_1 \gg T_2$  and the course of change of the relaxation times as a function of coverage give information regarding the adsorbate-adsorbent and adsorbate-adsorbate interactions and about the freedom of motion of the adsorbed molecules. At low surface coverages where no lateral interactions exist the molecules are adsorbed on the most active sites of adsorption. The minimum in  $T_1$  and the inflection point in the plot of  $T_2$  versus coverage seems to correspond to hydrogen bond formation between the adsorbed molecules and the OH groups of the surface<sup>3,4</sup>. The completion of the monolayer is followed by changes both in  $T_2$  and  $T_1$ . At higher coverages the properties of the adsorbed layers approach the properties of the liquid in bulk.

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## Relation between spectroscopic and lyotropic properties of ions in solution

D. MEYERSTEIN AND A. TREININ, *Department of Physical Chemistry, The Hebrew University of Jerusalem*

The electron transfer spectrum of  $\text{I}^-$  in solution is relatively very sensitive to environmental effects<sup>1</sup>. Its general behaviour towards addition of foreign solutes — electrolytes and non-electrolytes — indicates that their effect depends mainly on their ability to desolvate the test-ion  $\text{I}^-$ . For further support of this conclusion the study



was extended to include the effect of a large series of anions on the onset of the long wavelength band of  $I^-$ . A relation was found between the spectral shift caused by the foreign anion and its lyotropic number<sup>2</sup>.

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**Elastic properties of high surface area solid adsorbent**

Y. KOZIROVSKI AND M. FOLMAN, *Department of Chemistry, Technion-Israel Institute of Technology, Haifa*

In continuation of previous work<sup>1</sup>, the Young modulus of non-methylated and methylated porous Vycor glass was determined using a direct method. The measurements were done *in vacuo* by means of strain gauges, with an accuracy of  $1\mu$ -strain. The moduli obtained differed by about 10%. This difference was ascribed to the contribution of the hydrogen bonded OH groups present on the surface of the non-methylated adsorbent,

In order to calculate this contribution, a potential function for the hydrogen bond was chosen. From this function, the value of the force constant,  $k_{O...O}$ , of the O...O bond was obtained, using the experimental value of  $\Delta\nu$  — the shift in stretching frequency of the hydrogen bonded OH groups. The contribution to the Young modulus of the hydrogen bonds, obtained from the knowledge of the force constant and the number of OH bonds per  $cm^3$ , was in good agreement with the value from obtained from measurements.

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## CHEMICAL ENGINEERING

### Solar evaporation of copper sulfate at the Timna copper plant

E. BASEVI, *Israel Mining Industries-Laboratories*

Considerations of specific problems, e.g., corrosion, occlusion due to precipitation, scaling, thermal balances, handling of large volumes of solution and cost involved in concentration of copper sulfate solution containing Cu (3–4 g/l), calcium sulfate at saturation, phosphates ( $P_2O_5$  2–3 g/l.), ferrous sulfate and silica, have shown that solar evaporation is most advantageous for the first step of concentration. From among the known concentration methods the most practical and economical for this purpose is multiple effect evaporation, that is compared with solar evaporation. Results of experiments with solar evaporation in winter conditions have shown that an energy recovery of 680 kcal./sq.m/hr. during the period between sunrise and sunset is obtained. Of decisive importance is the incidence angle of the sun rays and not other climatic factors e.g., wind velocity, relative air humidity and air temperature. Technological plant features will be described. Results of experiments conducted during the summer will be given. The major factor in the operation is cleanliness of the surfaces, maintained by adjustment of the flow rate of the solutions. Maximum efficiency of evaporation is obtained by adjusting the thickness of the flowing solution layer and its rate of flow. Theoretical considerations of these factors will be discussed.

### Heat transfer by forced convection between a free liquid sheet and air in crossflow

I. YARON\* AND D. HASSON, *Department of Chemical Engineering, Technion-Israel Institute of Technology*

Heat transfer by forced convection between a vertical liquid sheet and air flowing parallel to it in a horizontal duct of circular cross section has been studied. Two-dimensional free sheets obtained from fan spray nozzles were used, having approximately a 5 sq. cm heat transfer area, 3 micron lower edge thickness and liquid velocities of about 15 m/sec. Low vapour pressure liquids, di-n-butyl phthalate (viscosity 26 cp.) and aqueous solutions of glycerol (2–9 cp.), were investigated. The preheated liquid was exposed to ambient air flowing in the duct, at velocities of 1.4 to 5 m/sec. Temperatures were measured by thermistors.

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\* This paper is part of a thesis submitted to the Senate of the Technion, Israel Institute of Technology, as a partial fulfilment of the requirements for the degree of M.Sc.

Overall mean heat transfer coefficients, based on temperatures of the sheet extremities, varied in the range of 30 to 400 K cal/hr. m<sup>2</sup> °C. These values correspond to a 10 fold increase for the glycerol solutions and 2 to 4 fold increase for the more viscous di-butyl phthalate, as compared with conventional laminar boundary layer heat transfer data for solid plates and wetted surfaces.

### **Percolation leaching of Timna copper ore**

A. MITZMAGER, J. FEIGLIN AND J.E. GAILIS, *Israel Mining Industries-Laboratories*

Laboratoryi semi-pilot and pilot tests in the Haifa laboratories of Israel Mining Industries resulted in the development of an upward percolation leaching process for coarse ore particles. This system will be tried out in a full size plant in Timna.

The process involves the classification, leaching and washing of Timna ore crushed to -6 mm particles.

The dry ore is fed continuously to a column where it comes in contact with an upward moving liquor. The slimes in this ore (approx. 40% of the total) overflow with the liquor to a separate leaching and washing system while the coarse particles settle into the column. On filling the column this coarse fraction is subjected to 6 hours of upward leaching by acid liquor followed by washing prior to discharge.

In the pilot plant trials, ore containing 1.6% copper was leached with 6% acid liquor to give a solution containing approximately 9 g/l of copper. The washed and leached particles had a residual copper content of 0.18% and the overall acid consumption was 4 parts by weight of acid to 1 part of copper.

No problems are encountered in discharging the columns' content, if removal of most of the -48 mesh particles takes place during the classification operation.

This system of leaching when operated semi-continuously in a column system in Timna, would result in considerable savings in operating costs as well as, in the increase of the leaching capacity of the whole plant for relatively small capital investment.

Details and technological problems of the process will be discussed.

### **A method of correlating binary azeotrope data**

L. M. SHORR, *Israel Mining Industries*

An empirical correlation of binary azeotrope data has been developed which can be



useful in predicting azeotrope formation and composition. The method is based upon the linear relationship found to exist between two compounds when the azeotrope compositions of each are compared with a series of functionally related compounds.

A number of examples will be presented.

### **A method for the evaluation of relative volatility of isotopes in ternary systems**

S. SIDERMAN\* AND J. GILADI, *Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa*

A method is proposed by which the relative volatility of isotopes in a ternary system can be evaluated.

The method is based on the relationship between the velocity of a component along a chromatographic column and its vapour pressure over the partitioning liquid in the column. Fractionation of the isotopes emerging out of the chromatographic column enables mass spectroscopic determination of concentrations. A mathematical procedure has been developed by which the relative volatility may be calculated.

The underlying assumptions as well the techniques and equipment used for the evaluation are presented.

### **The enrichment of $\text{H}_2\text{O}^{17}$ in packed distillation columns**

H. COHEN AND A. RAVIV, *The Weizmann Institute of Science, Rehovoth* and V. KLEIN AND D. MERANDA, *Israel Atomic Energy Commission, Rehovoth*

The fractionation of isotopes by distillation of a polynary mixture can be calculated with the help of a stage-by-stage method as described by Klein, Raviv and Fraenkel<sup>1</sup>.

A number of experiments was carried out on the separation of oxygen 17 from a mixture of enriched water in order to confirm the above mentioned method of calculation.

In order to obtain high concentrations of oxygen 17 in the column, the experiments were planned in accordance with results obtained by a computer calculation<sup>1</sup>.

The distillation column was filled with a tricomponent mixture of water ( $\text{H}_2\text{O}^{16}$ ,  $\text{H}_2\text{O}^{17}$ ,  $\text{H}_2\text{O}^{18}$ ), with known concentrations of the isotopes. After reaching steady-state conditions, the original mean concentration was changed without varying the

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\* This work is part of a thesis submitted to the Senate of the Technion-Israel Institute of Technology as partial fulfilment of the requirements for the degree of Doctor of Science.

total amount of liquid hold-up in the column, and once more steady-state conditions were obtained.

A number of experiments was done in the way described and the resultant concentration gradients were compared with the computed ones — good agreement between experimental and computed data was found and the maximum oxygen 17 concentration obtained (6%) was as predicted by the above mentioned calculation.

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### Multicomponent distillation — calculations of columns operating with feed and production, using a digital computer

A. RAVIV AND P. RABINOWITZ, *The Weizmann Institute of Science, Rehovoth*, and V. KLEIN, *Israel Atomic Energy Commission, Rehovoth*

The concentration gradient in columns under total reflux, for the separation of oxygen isotopes by distillation of water was calculated analytically by Y. Lehrer<sup>1</sup> and Kuhn<sup>2</sup>. A digital computer was used for the same calculations<sup>3</sup> and also for computations of ideal cascades for H<sub>2</sub>O<sup>17</sup> separation<sup>4,5</sup>. The aim of this work is the design of a tapered cascade operating with feed and production. The method used is a stage by stage computation starting with the feed point and calculating, by iterations, the enricher and stripper sections. These computing loops are repeated until isotope material balance is reached. The time needed to reach steady state conditions can be estimated from the number of necessary loops.

By this method one can control product concentrations when feed concentrations change, or vice versa.

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### Performance of different types of 1/4" Dixon rings in the separation of O<sup>18</sup> by water distillation

V. KLEIN, *Israel Atomic Energy Commission, Rehovoth*, AND A. RAVIV, *The Weizmann Institute of Science, Rehovoth*

One of the separation processes for the oxygen isotopes is by distillations of natural water in columns packed with Dixon rings<sup>1</sup>.

In the literature a great number of flooding and performance correlation can be found for different packings. In this work the characteristics of 1/4" Dixon rings made of various types of gauzes are investigated.

As is generally known, steady state operating conditions in distillations columns (i.e. constant flow and pressure drop) are reached much more easily for small flows than for larger ones. Therefore we aimed to establish correlations by which flooding velocities could be calculated from pressure drop data obtained for small flows.

The variation of H.E.T.P. with the flow in the range of 45–80% of the flooding velocity in the column was also investigated. It was found that the efficiency of the packing decreases as the flow increases.

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#### Performance of various diameter distillation columns packed with Dixon rings

D. MERANDA, *Israel Atomic Energy Commission, Rehovoth*, AND A. RAVIV, *The Weizmann Institute of Science, Rehovoth*

As a part of the D<sub>2</sub>O and H<sub>2</sub>O<sup>18</sup> projects, the performance of various diameter packed distillation columns was investigated. The research was carried out on 3"–30" diameter columns, packed with Dixon rings<sup>1</sup> of 1/4" and 1/8" diameter<sup>2</sup>.

The pressure drop as a function of through-put ( $\rho u^2$ ) at various pressures was determined and the flooding velocities as a function of the column pressure were obtained. In addition to the column behaviour experiments, HETP dependence on column and packing diameter as well as the height of packing was investigated.

A linear relationship between pressure drop and  $\rho u^2$  was found; where  $\rho$  and  $u$  are the vapor density and velocity. When  $\rho u^2$  is expressed in percent of maximum  $\rho u^2$

(at flooding), the pressure drop depends on the  $\left[ \frac{\rho u^2}{(\rho u^2)_{\max}} \right]$  ratio only.

It was found that at flooding, the quantity  $\rho u^2$  is constant and changes with the diameter of the packing only.

The HETP increases with both the column and packing diameter.

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### A new hydrochloric acid burner

E. KHERMOUSH, *Electrochemical Industries (Frutarom) Ltd., Haifa*

Graphite burners withstand thermal stresses and thus can be operated intermittently. A new type of graphite burner for the production of hydrochloric acid has been operated for the first time in the world by Electrochemical Industries (Frutarom) Ltd., Haifa.

The burner was designed by the Soc. Carbone Lo raine of France and Electrochemical Ind. and after making some changes it is operating for more than one year. Its advantages are:

- a) Wide range of capacity (50 to 210 kg/hr. of chlorine, with a very stable flame.
- b) Relatively small dimensions. All three operations, i.e. combustion, cooling of gas and water absorption to a 30% HCl solution, are made in one single compact unit.
- c) Extreme ease and safety in operation.
- d) Full utilization is made of the physical and chemical properties of graphite to obtain a pure acid.

A technical description of this new burner is given and a comparison is made with available units.

### The influence of organic liquids on aqueous solutions of inorganic salts

D.H. KOHN AND I. YARON, *Faculty of Chemistry and Chemical Engineering, Technion-Israel Institute of Technology, Haifa*

It has been noticed<sup>1</sup>, that the addition of an organic liquid to an aqueous solution of potassium bisulphate results in the precipitation of the corresponding neutral salt.

This phenomenon has been further investigated by studying the effects of the addition of partially and completely miscible alcohols and ketones, to aqueous solutions of sodium and potassium bisulphate.

The following variables were examined:

1. The ratio organic liquid/aqueous solution up to a ratio of 10 to 1.
2. Initial aqueous solution concentration in the range from 47 g/liter up to saturation.
3. Temperature in the range of 5°C to 40°C.

Results, expressed as total salt precipitation and acid salt-neutral salt conversion may be summarized as follows:

1. Both, precipitation and conversion vary exponentially with increasing values of organic liquid/aqueous solution ratio.
2. At a given ratio of organic liquid/aqueous solution, increase of the concentration of the initial solution results in a higher amount of precipitation.
3. Precipitation and conversion are favoured by low temperatures.
4. Precipitation and conversion of sodium and potassium bisulphate solutions show similar behaviour.
5. The extent of precipitation and conversion varies for the different organic liquids used.

Extension of this study to other systems and a review of possible applications will be presented at a later stage.

Acknowledgement: Thanks are due to Mrs. H. Datner-Feldstein and to Messrs. M. Hassid, Z. Karo, A. Kupferberg and S. Shmorak for carrying out the experimental work.

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### Effect of u.v. irradiation on corrosivity of aviation gasoline\*

S. BENTUR, M. BABITZ AND A.B. STERN, *Fuel Testing Laboratory, Technion-Israel Institute of Technology, Haifa*

In previous studies the authors observed several cases of aviation gasoline becoming corrosive on prolonged storage through the action of elementary sulphur, with partial or complete disappearance of this corrosivity on exposure to sunlight. In the present study this phenomenon was studied in greater detail.

The experimental procedure consisted in artificial irradiation of contaminated gasolines and pure hydrocarbons, followed by a study of the various changes in properties. Samples were tested for corrosivity at 50°C and 100°C, elementary sulphur, mercaptans, peroxides, existent gums and octane number.

In one series of experiments air-exposed gasoline contaminated with different amounts of elementary sulphur and mercaptans was subjected to varying periods of irradiation at 5 cm (2000–3000 Å wavelength) by means of an "Ultraviolet Products" Mineral Light lamp type R-51. These experiments showed that corrosivity of aviation gasoline can be reduced by irradiation. This reduction is related to peroxide formation, both being dependent on irradiation time: the higher the respective sulphur contents, the higher the corrosivity and the peroxide content required. For short irradiation times, all other properties remained within specification limits.

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\* Paper accepted for publication in "Journal of Chemical Engineering Data".

Another series dealt with the response to irradiation of the commonly used TEL and of an approved antioxidant inhibitor. Here again the presence of peroxides appears to be the decisive factor in reducing corrosivity, the most outstanding case being that of cyclohexene, where even the unirradiated hydrocarbon, with a high peroxide content, failed to show any effect on the copper strip and irradiation resulted in an appreciable decrease in both sulphur contents.

In saturated hydrocarbons the presence of TEL had a marked effect on peroxide formation, resulting in a decrease in both sulphur contents and corrosivity. Aromatics, on the other hand, behaved quite differently and appeared to be unaffected by irradiation even in the presence of TEL. In the case of contaminated benzene different discolouration of the copper strip was observed, for which no satisfactory explanation could be found.

A sample of naturally-contaminated aviation gasoline which had become corrosive on storage (2d by the 100°C test) was also subjected to irradiation. All corrosivity disappeared after less than 30 sec., the other properties remaining well within specification limits.

### **Development of a process for the utilization of sulphuric acid sludge.\***

B. GAL-OR\*\* AND J. GILADI, *Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa*

A new process has been developed for the production of aluminium sulphate and by-products from sulphuric acid sludge and clay. The process has been tested on a pilot plant scale with acid sludges from the petroleum and detergent industries. The novel features of the process involve the simultaneous reaction and steam distillation of the reaction products under pressure.

The process can be illustrated by the following example: Fresh sulphuric acid sludge from kerosene treatment is charged into an autoclave together with uncalcined flint clay and water. The temperature is gradually raised without allowing any reaction products to be removed from the autoclave. At 140°C steam, SO<sub>2</sub> and organic matter are steam distilled from the autoclave and conducted to a condenser while the reaction continues under pressure. The condensate is collected and the organic matter is separated for its organic by-product value. Pressure is allowed to increase

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\* An Israeli patent for this process was applied for on the 5th of Dec. 1960, under the number 14732.

\*\* This paper constitutes part of a thesis to be presented to the Senate of the Technion-Israel Institute of Technology, as a partial fulfilment of the requirement for the M.Sc. degree.



during the steam distillation. After the reaction is completed water is added and any undissolved matter is filtered off. The filtrate contains pure aluminium sulphate.

Although the process is carried out in one stage several reactions proceed in parallel: a) Clay is attacked by free  $\text{H}_2\text{SO}_4$  to form  $\text{Al}_2(\text{SO}_4)_3$ . b) Any sulphonic acids are hydrolysed into free  $\text{H}_2\text{SO}_4$  and organic matter. As a result of the steam distillation which removes the volatile organic matter the hydrolysis equilibrium is shifted so that it proceeds to completion. c) The clay residue is activated to a certain extent by the  $\text{H}_2\text{SO}_4$  and as a result it is capable of adsorbing impurities still remaining in the mixture. d) Trivalent iron is reduced to bivalent iron by the organic matter and  $\text{SO}_2$  with the result that no chemicals or other special treatment is necessary as is normal in the common processes for  $\text{Al}_2(\text{SO}_4)_3$  production.

The aluminium sulphate product is technically pure, and is ready for marketing without need for further purification. This process shows good promise of being an economic proposition, especially for small and medium scale refineries.

The research was proposed by Dr. G. Stern of "Fertilizers and Chemicals Ltd." The cooperation of the Research and Development Department of the C.R.L., Haifa and Dr. A. Gottesman are gratefully acknowledged.

### Activation of Israeli clay for adsorption purposes

B. GAL-OR, *Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa*

Activated clays are used mainly for decolourizing and removing of various impurities present in lubricating and vegetable oils. The possibility of chemical activation of Israeli clay was found in this work and the product obtained has high adsorptive power which is equal to or even higher than that of imported clays.

The steps in the activation process are: Crushing and grinding of the clay to the suitable mesh size, activation by mineral acid and live steam with effective agitation, washing by water or alkali until the suitable pH is obtained, filtration, drying and grinding. The main factors which influence the quality of the product are: Acid/clay ratio, acid concentration, reaction temperature, time of reaction, final pH, extent of drying, temperature of drying and final mesh-size. The quality of the product was determined by comparing its bleaching power on used lub-oils and vegetable oils with that of imported bleaching clays.

The Israeli clay originates in the Makhtesh Rammon. The mineralogic structure of this clay is montmorillonite and it was defined as Fuller's Earth. The existence of high quality Israeli active clay was not known and therefore it has not been exploited.

There is a large demand for high quality activated clays over the world and there-

fore it is reasonable to exploit the Israeli clay for domestic use (instead of these now imported) and for export. The process may be combined with the Aman process or with other processes which produce hydrochloric acid as a by-product. Production of this clay in Israel will reduce the surplus of HCl and increase the profitability of the planned lub-oil refinery.

This research was proposed by Ing. J. Giladi, senior lecturer in the Department of Chemical Engineering at the Technion.

### Flotation of chrysocolla ( $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$ )

A. MITZMAGER AND J.E. GAILIS\*, *Israel Mining Industries-Laboratories*

A literature survey on the direct flotation of chrysocolla revealed that the conventional methods for oxide minerals of the base metals are in general not satisfactory. Sulphidization produces a mechanically weak sulphide surface film which is usually scrubbed off during flotation. Fatty acid flotation is feasible but is very non-selective. Use of sulphydric collectors for chrysocolla has not been reported. The use of more specific collectors has proved to be more promising and encouraging results have been reported on synthetic ores using alkyl derivatives of polyhydroxy-nitroso-phenols and also with alkyl derivatives of triphenylmethane dyes.

Work on the Timna copper ore using various chelating reagents indicated that this type of collector, which is more or less specific to copper, shows promise. Hallimond tube tests showed that iso-octyl-thioglycollate, 2-mecapto-benzothiazole and 4-lauroyl-catechol are capable of floating pure chrysocolla. Flotation tests on synthetic ore containing 5% chrysocolla and 95% quartz, confirmed these results except that the film produced by iso-octyl-thioglycollate was scrubbed off. The other two reagents have recoveries of 85 to 95% of almost clean chrysocolla when using about 800g reagent per ton of ore. Tests on Timna ore gave negative results with marcaptobenzothiazol. Lauroyl-catechol displayed ability to collect the copper minerals, maximum recovery being 85% of the copper but the concentrate assay was a maximum of only 4.4% Cu as compared to 1.8% Cu in the feed. Collector consumption was of the order of 700g per ton of ore. High reagent consumption is attributed to the porous nature of the copper minerals and the tendency of the ore to disintegrate into slimes. Low concentrate assays are attributed to the inherent inability to obtain liberation of the copper minerals.

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\* This paper is part of a thesis submitted to the Senate of the Technion, Israel Institute of Technology, as partial fulfilment of the requirements for the degree of M.Sc.

## Extraction of uranium from calcined phosphate rock with one stage CaO slaking by aqueous sugar solutions

A. SHAMGAR, R. RAFAELOFF, A. WALTER AND M. LEVY, *Israel Atomic Energy Commission*

The tendency of uranyl hydroxide to form hydrosols is known<sup>1</sup>. It was also found that sugars prevent the precipitation of uranate in aqueous sodium hydroxide<sup>2</sup>. This latter reaction can be reversed. It is possible to cause solubilisation of the uranium in the calcined phosphate rock by using sugar solutions in one stage. In this case, it was easy to regenerate the sugar by precipitation of calcium carbonate with the carbon dioxide formed in the calcination of the phosphate.

The calcination of the phosphate rock was carried out in a laboratory furnace at 850°C for one hour. Aqueous sugar solutions at concentrations of 6% or 12% were used for the extraction of the uranium at solution: rock ratio 10:1 or 5:1. The calcined phosphate rock was poured into the solution without grinding, stirred for several hours and left to stand for a few additional hours; the total contact time was about 24 hours. At the end of the extraction, the suspension was filtered and the rock washed.

It is possible to regenerate the sugar solutions by two methods: a) Bubbling of carbon dioxide during the extraction with the decantation of the calcium carbonate formed. b) Bubbling of carbon dioxide into the solution after the filtration of the rock.

The yield of uranium is about 80%. The enriched phosphate rock contains about 38%  $P_2O_5$ ; the  $P_2O_5$  losses being about 0.2%.

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## The natural anhydride of the Negev as a building material. I. Chemical and physical properties

J. YOFE\* AND L. HELLER *Israel Standard Institution\*\**

$CaSO_4$  appears in nature in many chemical and crystallographic forms. When heated the dihydrate or gypsum ( $CaSO_4 \cdot 2H_2O$ ) loses  $1\frac{1}{2}$  mols of water and is transformed to half hydrate (plaster of Paris), which binds water quickly and is therefore used as a binder.

\* Present address : Israel Atomic Energy Commission Laboratories, Rehovoth, Israel.

\*\* Work carried out on behalf of the Israeli Scientific Council, 1953-55.



The different anhydrides ( $\text{CaSO}_4$ ) have the same chemical composition but differ from each other in their crystallographic structure as well as in their water-binding properties. The one which is dealt with here is the natural  $\beta$ -anhydride which binds water slowly and can be used as building material if properly milled, and adequate catalysts added.

Being a natural binder, it does not need heating and is therefore cheaper than portland cement and plaster of Paris (produced from gypsum).

Its structural properties are nearly as good as those of portland cement and much better than plaster of Paris. It can be used as a plaster, binder or in place of portland cement in concrete (anhydride concrete).

The work to be presented includes the theory of binding anhydride into gypsum, factors affecting binding time, effects of adding positive and negative catalysts, analytical methods for the determination of bound and free water and particle size. The genesis of the Negev anhydride will be discussed.

## **The natural anhydride of the Negev as a building material. II. Field experiments**

**J. YOFE\* AND L. HELLER** *Israel Standard Institution\*\**

Research on anhydride as a building material was started some 30 years ago by Budnikov in Asiatic Russia. A whole town was then built with this material, and after the war ruined cities in Germany were reconstructed with anhydride, as plaster and as concrete.

In 1953, the author, analysing some samples of gypsum from the Negev, found some of them to be anhydride. As a result of further investigation huge amounts of this material, were found in the Negev (especially in Yotvata and in Wadi-Ramon) with the help of the Army-Engineers. It was then suggested by the author that this material may be used as a binder for building work in Eilath, thus economizing both transportation and fuel for manufacturing, as there is no need to heat the raw material.

Three years of research by the author and his collaborators in the Israeli Standard Institution as well as a small anhydride plant built by the army in Eilath and finally the test building of some 200 houses (in 1950) in Eilath furnished practical information.

**ACKNOWLEDGMENT:** Thanks are due to Messrs. Tenny and Ben-Yair of the Building Material Dept., Standards Institution who participated actively in this work.

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\* Present address: Israel Atomic Energy Commission, Laboratories, Rehovoth, Israel.

\*\* Work carried out on behalf of the Israeli Scientific Council, 1953-55.

## Cold alkali pulping of eucalyptus wood

MENACHEM LEWIN, AVRAHAM LENGYEL AND BERNARD TOKER, *Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem*

The wood of *Eucalyptus rostrata* and *Eucalyptus gomphocephala* that is being grown in Israel is known to be of high density — 0.50 and 0.64 g/cm<sup>3</sup> and the fibres to be relatively short — 0.85 and 0.71mm, respectively. While it has been shown previously that *E. rostrata* can be advantageously pulped by the kraft (sulphate) process only low yields and inferior quality pulps can be obtained by this process from *E. gomphocephala*. The present work deals with cold alkali pulping of these species in order to check on the possibility of obtaining mechanical pulp which could be used in the preparation of newsprint.

Specimens of 6 year old *E. rostrata* from Hadera and of *E. gomphocephala* from Esht'ol were used in the experiments. The wood was impregnated with 4% of 5% NaOH (calculated on oven dry wood), for 2 hours at a hydrostatic pressure of 5 atmospheres, at room temperature. The refining was done in the Sprout-Waldron refiner. The energy consumed was 50 HP day/ton. The pulp yield amounted to 90% o.d. on o.d. for both wood species. The mechanical strength properties of the cold alkali pulps from *E. rostrata* and *E. gomphocephala* were respectively: tear factor — 36 and 24g; breaking load — 1400 and 1100 meters; burst factor — 7 and 4 kg/cm<sup>2</sup>; all data at a 300 ml Canadian Standard Freeness beating level.

The reddish colour of *E. rostrata* pulp and the yellowish colour of the *E. gomphocephala* pulps presented some difficulties in bleaching, but when bleaching in one stage with 10–15% calcium hypochlorite, brightnesses of 58–60% and 60–62% G.E. were obtained for the pulps from both species, respectively.

Blending the pulps with 20% sulphite spruce pulp, to obtain newsprint, improved the strength properties as follows: tear factor — 88 g for *E. rostrata* and 104 g for *E. gomphocephala*; breaking load — 2300 and 1600 meters; burst factor — 12 and 7 kg/cm<sup>2</sup>.

The blending improved the brightness, measured spectrophotometrically, of *E. gomphocephala* to 64% but did not improve it for *E. rostrata*.

The above results point to the feasibility of producing groundwood grade pulp in Israel for newsprint from local raw material.

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יוצא לאור ע"י  
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